DR



# N THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Donald R. Huffman, et al.

**Examiner:** 

Susy N. Tsang-Foster

Serial No.:

07/580,246

Art Unit:

1745

Filed:

September 10, 1990

Docket:

7913Z

For:

**NEW FORM OF CARBON** 

Dated:

October 10, 2007

Confirmation No. 5441

Mail Stop Amendment Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

# SUBMISSION FOR ACCORDING RESPONSE AS BEING TIMELY FILED PURSUANT TO 37 C.F.R. §1.8

Sir:

Pursuant to the provisions of 37 C.F.R. §1.8, a complete Response to the Office Communication dated June 8, 2007 ("Office Communication") was duly filed with the United States Patent and Trademark Office ("USPTO") on September 4, 2007. However, Examiner Tsang-Foster has advised applicants' attorney in a telephone interview on October 1, 2007 that the Response was not found in the USPTO; Examiner Tsang-Foster questioned whether a Response was filed.

In accordance with the provisions of 37 C.F.R. §1.8(b), applicants are hereby requesting that the filing of the above-identified Response consisting of the documents listed hereinbelow be considered timely. In support thereof, and as evidence of the applicants' response to the Office Communication, applicants are submitting another copy of the documents that were deposited with the United States Postal Service in a prepaid envelope addressed to: Mail Stop

Amendment, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on September 4, 2007. A copy of the documents that were mailed to the USPTO on September 4, 2007, is annexed hereto and is made a part hereof as Exhibit A. A list of the documents is as follows:

- 1. Transmittal Letter
- 2. Communication dated September 4, 2007, referring to all of the declarations listed in Items 4-6 hereinbelow
- Certificate of Mailing dated September 4, 2007 as part of the Transmittal
   Letter and Communication referred to in Items 2 and 3
- 4. Declaration of Harold W. Kroto pursuant to 37 C.F.R. §1.132 executed on August 27, 2007, having 13 exhibits attached thereto\*
- 5. Declaration of Mauricio Terrones pursuant to 37 C.F.R. §1.132, executed on August 28, 2007, having three exhibits attached thereto\*
- Declaration of Adam Darwish pursuant to 37 C.F.R. §1.132 dated August
   28, 2007, having 16 exhibits attached thereto\*
- 7. A postcard which lists the documents that were mailed on September 4, 2007

It is to be noted that a Response to the Office Communication was due on September 8, 2007.\*\*

It is to be noted that these declarations were filed in three other applications. Reference in these declarations is to Serial No. 08/236,933.

Inasmuch as September 8, 2007 was a Saturday, in accordance with 37 C.F.R. §1.7, a Response was actually due on September 10, 2007.

As evidence of the timely mailing of the Response, attention is directed to the Certificate of Mailing identified in Item 3 hereinabove. This certificate certifies that the Transmittal Letter identifying the items that were being transmitted to the USPTO on September 4, 2007, with the mailing, viz., Items 2-6 listed hereinabove, including the Communication, were deposited as first class mail in an envelope addressed to the Commission of Patents. A review of the documents filed clearly establishes that these documents constitute a complete Response to the outstanding Office Action. In view of the certification in the 2 Certificates of Mailing, a complete Response was timely mailed to the USPTO.

As further evidence that the applicants timely fled a Response to the Office Communication, applicants direct the attention of the USPTO to a copy of the postcard listed in item 7. The postcard lists the items that were being forwarded to the USPTO on September 4, 2007, namely, the Communication identified in Item 2, the Transmittal Letter identified in Item 1, the Certificate of Mailing in Item 3 and the Declarations identified in Items 4-6. A copy of the postcard is attached hereto as Exhibit B. In particular, attention is directed to the postmark stamped on back of the postcard. As clearly indicated, the postcard was stamped by the USPTO on September 7, 2007, which date is prior to the due date. Since the postcard accompanied the papers listed in items 1-6 hereinabove and since the postcard listed the documents identified in Items 1-6, this acknowledgement by the USPTO not only constitutes evidence that a complete Response to the Office Communication, i.e., the documents referred to hereinabove, was timely mailed to the USPTO, but also that these documents were received by the USPTO prior to the due date.

Since the above-identified documents were mailed in accordance with 37 C.F.R. §1.8(a) prior to the due date, the documents were timely field with the USPTO.

Finally, in accordance with the provisions of 37 C.F.R. §1.8, applicants' attorney enclose a verified statement by Mark J. Cohen, the attorney who prepared the Response entitled "Communication" and who attached the Communication to the three Declarations and the Transmittal Letter referred to hereinabove for filing in the USPTO. The declaration avers that the mailing was effected on the date certified, i.e., September 4, 2007, by having the above-identified documents deposited with the United States Postal Services as first class mail in an envelope addressed to Mail Stop Amendment, Commissioner for Patents, P.O. Box 1450, Alexandria, Va. 22313-1450. This Declaration is annexed hereto and made a part hereof as Exhibit C.

The submission is deemed to be in full compliance with the requirements of 37 C.F.R. §1.8(b). Accordingly, it is respectfully submitted that a complete Response was timely filed on September 4, 2007. Consequently, it is respectfully requested that the USPTO accord the filing of the enclosed copy of the Response as timely.

A Petition Fee is not expressly required under the controlling provisions of 37 C.F.R. §1.8(b). Authorization is given, however, to charge payment of any necessary fees associated with this Communication to Deposit Account No. 19-1013/SSMP. A duplicate copy of this paper is enclosed.

Respectfully submitted,

Mark J. Cohe

Registration No. 32,211

Scully, Scott, Murphy & Presser, P.C. 400 Garden City Plaza-Suite 300 Garden City, New York 11530 (516) 742-4343

MJC:htj

CERTIFICATE O		Docket No. 7913Z		
Application No. 07/580,246	Filing Date September 10, 19990	Examiner Tsang Foster, S.N.	Customer No. 23389	Group Art Uni 1754
OCT. 1.2 2007	RM OF CARBON			
TRADEMAR				
I hereby certify that	the following corresponde	nce:		
SUBMISSION FOR	ACCORDING RESPONS	E AS BEING TIMELY FILED PUR	SUANT TO 37 C.I	F.R. §1.8
	· (Ia	lentify type of correspondence)		
is being deposited v	vith the United States Pos	tal Service "Express Mail Post Office	e to Addressee" s	ervice under 37
CFR 1.10 in an enve	.1			
	elope addressed to: Comr	nissioner for Patents, P.O. Box 1450	), Alexandria, VA	22313-1450 on
	October 12, 2007	nissioner for Patents, P.O. Box 1450	), Alexandria, VA	22313-1450 on
_		nissioner for Patents, P.O. Box 1450	), Alexandria, VA	22313-1450 on
_	October 12, 2007	Mark J	. Cohen	
	October 12, 2007	<del></del>	. Cohen	
	October 12, 2007	Mark J	. Cohen son Mailing Correspond	
	October 12, 2007	Mark J (Typed or Printed Name of Person Ma (Signature of Person Ma	. Cohen son Mailing Correspond tiling Correspondence)	
	October 12, 2007	Mark J (Typed or Printed Name of Person Ma	. Cohen son Mailing Correspond tiling Correspondence)	
	October 12, 2007	Mark J (Typed or Printed Name of Person Ma (Signature of Person Ma	. Cohen son Mailing Correspond tiling Correspondence)	
	October 12, 2007	Mark J (Typed or Printed Name of Person Ma (Signature of Person Ma	. Cohen son Mailing Correspond tiling Correspondence)	
	October 12, 2007 (Date)	Mark J  (Typed or Printed Name off Person Ma  (Signature of Person Ma  EM 06686  ("Express Mail" Main	. Cohen son Mailing Correspond uiling Correspondence) 556648 US ling Label Number)	
<u>-</u>	October 12, 2007 (Date)	Mark J (Typed or Printed Name of Person Ma (Signature of Person Ma	. Cohen son Mailing Correspond uiling Correspondence) 556648 US ling Label Number)	
	October 12, 2007 (Date)	Mark J  (Typed or Printed Name off Person Ma  (Signature of Person Ma  EM 06686  ("Express Mail" Main	. Cohen son Mailing Correspond uiling Correspondence) 556648 US ling Label Number)	

	TRANSMIT (General - F	Docket No. 7913Z						
In Re Application Of: Donald R. Huffman, et al.								
Application No.	Filing Date	Examiner	Customer No.	Group Art Unit	Confirmation No.			
07/580,246	September 10, 1990	Tsang Foster, S.N.	23389	1754	5441			
Title: ONEW FORM OF CARBON  OCT. 1.2 2007								
PRADEMA	<del></del>	COMMISSIONER FOR PATI	ENTS:					
Transmitted herew	vith is:							
<ol> <li>General Transmittal in Duplicate</li> <li>Submission for According Response as being timely filed (in duplicate)</li> <li>Exhibit A consisting of copies of Transmittal Letter of September 4, 2007, Communication dated September 4, 2007, Declarations of Harold Kroto, Mauricio Terrones and Adam         <ul> <li>Darwish, Certificate of Mailing dated September 4, 2007, Copy of postcard dated September 4, 2007.</li> </ul> </li> <li>Exhibit B consisting of copy of postcard dated 9/4/2007</li> <li>Exhibit C consisting of Declaration of Mark J. Cohen (6) Certificate of Express Mail No. EM 066865648</li> <li>in the above identified application.</li> </ol>								
<ul> <li>No additional fee is required.</li> <li>A check in the amount of is attached.</li> <li>The Director is hereby authorized to charge and credit Deposit Account No. 19-1013/SSMP as described below.</li> <li>Charge the amount of</li> <li>Credit any overpayment.</li> <li>Charge any additional fee required.</li> <li>Payment by credit card. Form PTO-2038 is attached.</li> <li>WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.</li> </ul>								
Mark J. Cohen Registration No. 32 Scully, Scott, Murph			Dated: Octob		spondence is being			
400 Garden City Pla Garden City, New Y (516) 742-4343	aza, Suite 300		deposited with sufficient postar addressed to th	n the United States ge as first class he "Commissioner f a, VA 22313-1450" [3	s Postal Service with mail in an envelope for Patents, P.O. Box			
cc:			Signatur	re of Person Mailing C	Torrespondence			

Typed or Printed Name of Person Mailing Correspondence

# PATENT OFFICE DATE STAMP WILL ACKNOWLEDGE RECEIPT OF:

- General Transmittal Letter (in duplicate)
- Communication
- Declaration of Harold W. Kroto Pursuant to 37 C.F.R. §1.132 (Exhibits 1-13) 3.
- Declaration of Mauricio Terrones Pursuant to 37 C.F.R. §1.132 (Exhibits 1-3)
- 5. Declaration of Adam Darwish Pursuant to 37 C.F.R. §1.132 (Exhibits 1-16)
- 6. Certificate of Mailing dated 9/4/07

Applicants: Donald R. Huffman, et al.

Serial No.:

07/580,246

Filed:

September 10, 1990

For:

NEW FORM OF CARBON

Docket:

7913Z

Dated:

September 4, 2007

MJC:dg

SEP U 7 2007

#### TRANSMITTAL LETTER Docket No. (General - Patent Pending) 7913Z In Re Application Of: Donald R. Huffman, et al. Application No. Filing Date Examiner Customer No. Group Art Unit Confirmation No. 07/580,246 **September 10, 1990** Susy N. Tsang Foster 23389 1745 5441 Title: **NEW FORM OF CARBON COMMISSIONER FOR PATENTS:** Transmitted herewith is: **COMMUNICATION** DECLARATION OF HAROLD W. KROTO PURSUANT TO 37 C.F.R. §1.132 (EXHIBITS 1-13) DECLARATION OF MAURICIO TERRONES PURSUANT TO 37 C.F.R. §1.132 (EXHIBITS 1-3) DECLARATION OF ADAM DARWISH PURSUANT TO 37 C.F.R. §1.132 (EXHIBITS 1-16) in the above identified application. $\boxtimes$ No additional fee is required. A check in the amount of is attached. The Director is hereby authorized to charge and credit Deposit Account No. 19-1013/SSMP as described below. Charge the amount of $\boxtimes$ Credit any overpayment. Charge any additional fee required. ☐ Payment by credit card. Form PTO-2038 is attached. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038. Dated: September 4, 2007 Signature Mark J. Cohen Registration No. 32,211 Scully, Scott, Murphy & Presser, P.C. I hereby certify that this correspondence is being 400 Garden City Plaza, Suite 300 deposited with the United States Postal Service with sufficient postage as first class mail in an envelope Garden City, New York 11530 addressed to the "Commissioner for Patents, P.O. Box 516-742-4343 1450, Alexandria, VA 22313, 1450 [37 CFR 1.8(a)] on September 4, 2067 (Date an Signature of Person Mailing Correspondence

MJC:dg

Mark J. Cohen

Typed or Printed Name of Person Mailing Correspondence

# IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Donald R. Huffman, et al.

Examiner:

Susy N. Tsang-Foster

Serial No.:

07/580,246

Art Unit:

1745

Filed:

September 10, 1990

Docket:

7913Z

For:

**NEW FORM OF CARBON** 

Dated:

September 4, 2007

Confirmation No. 5441

Mail Stop Amendment Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

**COMMUNICATION** 

Sir:

In response to the Office Communication dated June 8, 2007 ("Official Communication"), applicants submit the following Remarks for entry in the above-identified application. The Remarks commence on page 2 of this Communication.

**CERTIFICATE OF MAILING UNDER 37 C.F.R. §1.8(a)** 

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Mail Stop Amendment, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Dated: September 4, 2007

#### **REMARKS**

The Official Communication dated June 8, 2007, from the United States Patent and Trademark Office ("USPTO") suspended prosecution for a period of three months to permit applicants to submit additional evidence in support of the patentability of the present application.

Claims 53-73, 75, 80, 81, 84-86, 89, 90, 92-96, 102-107, 111-114, 119, 122-132, 141-157, 162 and 165-170 are pending in the above-identified application. Claims 85, 90, 94 and 95 have been allowed. The remaining claims have been rejected and are on appeal. The Examiner's Answer, *inter alia*, rejected Claims 53-72, 86, 96, 102-107, 111-114, 119, 122-132, 141-152, 154-157, 162 and 165-170 under 35 U.S.C. §112, first paragraph, for allegedly failing to comply with the written description requirement for the term "macroscopic", as it relates to C<sub>60</sub> and C<sub>70</sub>, either in the product or in the soot. <sup>1</sup>

Applicants respectfully disagree. Contrary to the allegations of the USPTO, the present application provides adequate support for the term "macroscopic amounts", as it relates to C<sub>60</sub> and C<sub>70</sub>, in accordance with the provisions of 35 U.S.C. §112, first paragraph. In support, applicants are submitting, as evidence, the executed Declarations of Drs. Terrones ("Terrones Declaration"), Darwish ("Darwish Declarations") and Kroto ("Kroto Declaration").

These Remarks and the attached Declarations are intended to supplement earlier filed Remarks and Declarations and other evidence previously submitted during the prosecution of the above-identified application and/or parent applications thereof and are not intended to replace any of these.

Other issues raised in the Examiner's Answer have been addressed on the record, including the Appeal Brief, and are incorporated herein by reference.

It is to be noted that these aforesaid Declarations are based upon the disclosure in USSN 08/236,933. The above-identified application has the same disclosure as USSN 08/236,933; thus, the testimony thereon is also applicable to the above-identified application.

The Three Declarations submitted provide additional evidence that the above-identified application complies with the enablement and description requirements of 35 U.S.C. §112, first paragraph.

Dr. Terrones testified in the Terrones Declaration that the experiments were conducted exactly as described in Examples 1 and 2 of the '933 application. As testified by Dr. Terrones, he built a bell jar apparatus which was identical to the one described in the '933 application. (Paragraphs 6 and 8 of the Terrones Declaration). However, the bell jar apparatus built by Dr. Terrones had one constraint; the vaporization could only be conducted for about 2 minutes. (Paragraphs 8 of Terrones Declaration). Nevertheless, as Dr. Terrones has testified, the vaporization of graphite was conducted in accordance with the procedure described in the '933 application. Id. More specifically, as testified by Dr. Terrones in Paragraph 10 of the Terrones Declaration, the bell jar apparatus was evacuated to 10<sup>-4</sup> torr, and filled with high purity helium. Pure graphite rods of 1/4" in diameter were utilized in the experiments conducted, wherein a onecentimeter length of the tip of each rod was reduced in diameter to about 5 millimeters, in accordance with the procedure described in the '933 application. Id. The graphite rods were evaporated by resistive heating at 100 torr helium using a current of 100 amps for about 2 minutes. Id. The vaporization of the graphite rods was collected on a substrate, an aluminum sheet (used as a collector), having a semicircular configuration, placed about 4.7 cm from the bottom of, 7.57 cm to the right of, and 11 cm from the top of, the evaporating carbon rods. Id. The bell jar apparatus was opened after a cooling down period of 20 minutes, and the black soot

that was formed was removed by scraping the soot from the substrate surfaces and internal surfaces of the bell jar apparatus. <u>Id</u>.

On average, about 100 mg. of soot was collected from each run (Terrones Declaration, Paragraph 10). Dr. Terrones testified that the procedure was repeated until 1 gram of soot was collected. <u>Id</u>.

Dr. Terrones conducted another experiment in which he vaporized the graphite rods at two atmospheres, using a current of 100 amps (Paragraphs 8 and 13 of Terrones Declaration). However, he had to make a modification of the bell jar apparatus to conduct the experiment at the higher pressure. <u>Id</u>. As testified in Paragraph 8 of Dr. Terrones Declaration, Dr. Terrones modified the bell jar apparatus described hereinabove by replacing the glass cover of the bell jar apparatus with an aluminum cover, which was adapted with stoppers and bolts/nuts to keep the aluminum cover in place for high-pressure operation. Further as indicated in Paragraph 8 of his Declaration, this "aluminum reactor" was equivalent to the bell jar apparatus in the '933 application.

Dr. Terrones testified that the vaporization of graphite rods at 2 atm pressure and 100 amps was identical to the procedure described hereinabove, except that the aluminum reactor was used instead of the bell jar apparatus and the vaporization was conducted for about 1 minute, divided into three time periods of 25 seconds, 13 seconds and 22 seconds (Paragraph 13 of Terrones Declaration). In addition, there was no attempt to amass the soot at the higher pressure to obtain a large amount of soot, as performed for the lower pressure experiments. Paragraph 14 of Terrones Declaration. About 100 mg of soot was collected (Paragraph 13 of Terrones Declaration). Both the 1-gram sample of soot and 100 mg sample of soot were forwarded to Dr.

Darwish for separation of the fullerenes therefrom (see Paragraphs 10 and 14 of Terrones Declaration).

Dr. Darwish testified that he separated various fullerenes from the two samples, including C<sub>60</sub> and C<sub>70</sub>, using techniques that were either known to one of ordinary skill in the art on August 30, 1990, (the filing date of USSN 07/575,254, the parent application) or described in the '933 application. More specifically, he utilized a soxhlet extractor using toluene as the solvent. (Paragraph 7 of Darwish Declaration). Dr. Darwish collected about 10% soot extract. Id. Various fullerenes were obtained from the soot extract, as described in Paragraph 7 of the Darwish Declaration, by utilizing preparative HPLC under the following conditions: Cosmosil 5µm PYE column (250mm x 10mm), HPLC-grade toluene as the solvent, eluted from the column at a rate of 4 ml/min. Id. The fractions eluting from the column exhibiting an absorbance at 285 nm were collected. Id. From the 1-gram sample of soot prepared from the vaporization of graphite rods at 100 torr, about 65 mg of C<sub>60</sub> crystals and 15 mg of C<sub>70</sub> crystals were collected. Paragraph 9 of Darwish Declaration. As testified in Paragraphs 12 and 13 of the Darwish Declaration, the C<sub>60</sub> and C<sub>70</sub> that were isolated from the soot were seen with the naked eye. (See also Exhibits 3 and 4, respectively).

Dr. Darwish also separated, inter alia, C<sub>60</sub> and C<sub>70</sub> from the 100 mg sample of soot that was produced from the vaporization of graphite at 2 atmosphere utilizing the same procedure as outlined above. See Paragraph 23 of Darwish Declaration. Dr. Darwish obtained 9% yield from the soot. Id. Dr. Darwish obtained 5.0 mg of C<sub>60</sub> and 1.5 mg of C<sub>70</sub> from the soot produced at 2 atm from the 100 mg sample of soot (Paragraphs 24 and 25 of Darwish Declaration).

Further, the  $C_{60}$  and  $C_{70}$  collected from the vaporization of graphite at 2 atm were also present in amounts that could be seen with the naked eye (Paragraphs 24 and 25 of Darwish Declaration and Exhibits 13 and 14 attached thereto).

The testimony of Dr. Kroto is an overall summary of the experimental work of Drs. Terrones and Darwish. Dr. Kroto testified that since C<sub>60</sub> and C<sub>70</sub> isolated by Dr. Darwish from various soots, which were produced from the vaporization of graphite at 2 atm and 100 torr, respectively, via resistive heating conducted by Dr. Terrones, were seen with the naked eye, the C<sub>60</sub> and C<sub>70</sub> were produced in both instances in macroscopic amounts (Paragraphs 20-22 and 27-28 of Kroto Declaration). Furthermore, as Dr. Kroto testified, the yield of fullerenes recovered from the soot prepared in accordance with the procedure described in the '933 application is about 10%, which is among the highest yield of fullerenes obtained from soot to date. (Paragraph 34 of Kroto Declaration). Moreover, as Dr. Kroto testified, the soots were prepared by following the procedure described in the '933 application, without an undue amount of experimentation (Paragraph 35 of Kroto Declaration). Further, as testified by Dr. Kroto, the methodology of separating the fullerenes, including C<sub>60</sub> and C<sub>70</sub> from the soot, was routine to the skilled artisan on August 30, 1990. Id. Thus, the process described in the '933 application was enabling for one of ordinary skill in the art on August 30, 1990 (the effective filing date of the present application) to make macroscopic amounts of C<sub>60</sub> and C<sub>70</sub> without undue amount of experimentation. Id.

The instant specification also provides descriptive support for producing macroscopic amounts of  $C_{60}$  and  $C_{70}$ . Case law has held that to comply with the written description requirements under 35 U.S.C. §112, first paragraph, the application must convey with reasonable clarity to the skilled artisan that as of the filing date the applicant was in

possession of the invention. <u>Vas-Cath Inc. v. Mahurkar</u>, 935 F.2d 1555, 1563-64, 19 USPQ 2d 1111, 1117 (Fed. Cir. 1991). The testimony of Drs. Terrones and Darwish and Dr. Kroto evidences that a person of ordinary skill in the art obtains macroscopic amounts of C<sub>60</sub> and C<sub>70</sub> following the procedure described in the above-identified application. The procurement of macroscopic amounts of C<sub>60</sub> and C<sub>70</sub> by the skilled artisan following the procedure described in the '933 application evidences that the applicants had possession at the time of filing the instant application of a process for preparing macroscopic amounts of C<sub>60</sub> and C<sub>70</sub>, as claimed.

These results reinforce the statements made by Dr. Kroto in his previous Declarations in which he testified that by following the procedure described in the application, he was able to prepare fullerenes, including  $C_{60}$  and  $C_{70}$ , in macroscopic amounts. (Paragraph 9 of Kroto Declaration).

Consequently, in view of the remarks herein and the Declarations of Drs. Kroto, Terrones and Darwish, it is respectfully submitted that the present case is in condition for allowance, which action is earnestly solicited.

Respectfully submitted,

Mark J. Collen

Registration No. 32,211

Scully, Scott, Murphy & Presser, P.C. 400 Garden City Plaza-Suite 300 Garden City, New York 11530 (516) 742-4343 Enclosure

MJC:htj/dg

#### IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Donald R. Huffman, et al.

**Examiner:** Tsang Foster, S.N.

**Serial No.:** 08/236,933

**Art Unit:** 1754

Filed:

May 2, 1994

Docket:

7913ZAZY

For:

**NEW FORM OF CARBON** 

Confirmation No.: 4115

Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

# DECLARATION OF HAROLD W. KROTO PURSUANT TO 37 C.F.R. §1.132

Sir:

I, HAROLD W. KROTO, declare and say as follows:

1. I am currently a Professor in the Department of Chemistry and Biochemistry at the Florida State University in Tallahassee, Florida. I am also the Royal Society Research Professor in the School of Chemistry and Molecular Sciences at the University of Sussex, Brighton, United Kingdom (one of only twenty such appointments in the United Kingdom). Further, I am a visiting Professor at UCSB. Moreover, I have been awarded over one dozen honorary degrees from various universities. In 1996, I, along with Robert Curl and Richard Smalley, received the Nobel Prize in Chemistry for our discovery of fullerenes. Earlier that year, I was also awarded Knighthood for my contributions to chemistry. For the convenience of the United States Patent and Trademark Office, I have attached hereto as Exhibit 1 my curriculum vitae, which describe my credentials and demonstrate my expertise in the area of fullerenes.

- 2. I am intimately familiar with the literature concerning and was personally involved in the search for, C<sub>60</sub> and other fullerenes. I have written several articles on the subject, as evidenced by the publications listed in Exhibit 2, including the first definitive and only complete review on the subject in Kroto, et al., in <u>Chemical Review 1991</u>, 91, 1213 1235. I therefore believe that I am among the recognized experts on the subject of fullerenes.
- 3. In preparing this Declaration, I have read and reviewed the subject patent application, i.e., USSN 08/236,933 in its entirety ("'933 application"), including the pending claims, which are directed to, among other things, a process for making  $C_{60}$  and  $C_{70}$  in macroscopic amounts. I have been advised that there is a companion application, USSN 486,669 ("'669 application"), on file in the United States Patent and Trademark Office. I have also been advised that, except for the claims, the disclosure in the '669 application is identical to that of the '933 application. It is my understanding that the claims in the '669 application are directed to, among other things, a process for making fullerenes in macroscopic amounts. I have also been advised of the pendency of two additional applications, namely USSN 580,246 (" '246 application") and USSN 471,890 ("'890 application"). It is my understanding that the claims of the '246 application are directed to, among other things,  $C_{60}$  and  $C_{70}$  in macroscopic amounts, while the claims of the '890 application are directed to, among other things, fullerenes in macroscopic amounts. It is my further understanding that, except for the claims, the respective disclosures are not only identical, but are also identical to the disclosure of the '933 application. I have been instructed to review the '933 application as one of ordinary skill in the art would read the application on August 30, 1990.
- 4. It is my opinion that the term "macroscopic amounts", as used in the claims of the '933 application, was clearly understood by one of ordinary skill in the art in 1990 at the time

of the filing of the first application in the lineage. It is my understanding that this term in the claims of the '933 application is used in its plain and ordinary meaning to connote that the process described therein produces fullerenes, including, for example, C<sub>60</sub>, in amounts, which can be seen easily with the naked eye. This is consistent with the definition of "macroscopic", as defined in the McGraw Hill Dictionary of Scientific Terms, 4<sup>th</sup> ed., p.1125, 1989, where the term is defined as "large enough to be observed by the naked eye," and in Hackh's Chemical Dictionary, 4<sup>th</sup> ed., wherein it defines "macroscopic" as describing "objects visible to the naked eye."

- 5. "Fullerenes", in my opinion, is a term of art that is also widely understood by the scientific community; it was adopted to conveniently describe the family of caged carbon molecules, as exemplified by C<sub>60</sub>. See, e.g. the section entitled "Fullerene" in the Concise Encyclopedia of Science and Technology, 3rd ed., Sybil P. Parker, ed., McGraw Hill, NY, NY, p.819 (1994), attached hereto as Exhibit 3. This section, which I prepared, defines fullerenes as an even number of carbon atoms arranged in a closed hollow cage, and specifically exemplifies fullerene-60 or C<sub>60</sub>, as a species of fullerenes. However, there are other species of fullerenes, and many of those can and have been prepared by the process described in the '933 application in macroscopic amounts.
- 6. This Declaration supplements (and is not intended to replace) the previous Declarations, which were executed on July 27, 1995 and June 9, 1995, and November 16, 1999, the contents of all of which are incorporated herein by reference.
- 7. I have been requested by applicants' attorney to supplement the Declarations identified in Paragraph 6. In particular, I have been asked to repeat the experiments as described in the '933 application and to describe in more detail, relative to the aforementioned

Declarations, the protocols used and the evidence obtained therefrom that show that fullerenes, for example,  $C_{60}$  and  $C_{70}$ , are produced, in accordance with the teachings in the '933 application, in macroscopic amounts.

- 8. In particular, I have been requested by applicants' attorney to prepare the fullerenes in accordance with the procedure described in the '933 application at two different pressures, viz., at 100 torr and 2 atm pressure.
- 9. I have repeated the experiments described in the '933 application several times prior to the most recent request by applicants' attorney, and as indicated in my earlier testimony, macroscopic amounts of C<sub>60</sub> and C<sub>70</sub> and other fullerenes have been produced in accordance with the procedure described therein. This testimony in this Declaration confirms my earlier testimony provided in the aforementioned Declarations.
- 10. Initially, it is to be noted, that the bell jar apparatus, described in the '933 application, is no longer being utilized today; thus the apparatus for preparing fullerenes had to be set up, in accordance with the teachings in the '933 application, before experiments in this endeavor were commenced.
- 11. Moreover, I no longer am conducting research in the fullerene area. In particular, my laboratory is no longer equipped to produce fullerenes.
- 12. I so advised applicants' counsel, and it was agreed that I would coordinate the performance of the requested experiments by colleagues of mine.
- 13. I instructed Mauricio Terrones in Mexico ("Dr. Terrones") to prepare the soot in accordance with the procedure described in the '933 application and especially Example 1 in the '933 application.

- 14. Dr. Terrones set up the bell jar apparatus as described in the '933 application for the vaporization of the graphite rods. It is my understanding that this bell jar apparatus used by Dr. Terrones was identical in every way to the bell jar apparatus described in the '933 application. However, it had one constraint. The vaporization to form the soot could only be conducted for at most about 2 minutes per run at 100 torr. Moreover, to conduct the vaporization at the higher pressure, i.e., 2 atm, the bell jar apparatus was modified by replacing the glass cover with an aluminum cover, which was adopted with stoppers and bolts/nuts to keep the aluminum cover in place (hereinafter this modified bell jar apparatus will be referred to as an "aluminum reactor"). This aluminum reactor was equivalent to the bell jar apparatus described in the '933 application. However, this aluminum reactor also had the same constraints, as the bell jar apparatus described above, except that vaporization conducted at 2 atm was performed in two to three segments, each no longer than about 25 seconds at a time.
- 15. Dr. Terrones conducted the experiments to produce the soot in accordance with the procedure described in the '933 application, and especially Examples 1 and 2, thereof, at two different pressures, one at 2 atm and the other at 100 torr, using a current of about 100 amps. Dr. Terrones vaporized graphite rods of ¼ inch in diameter, with a one-centimeter length of the tip of each rod being reduced in diameter to about 5 millimeters, at 100 torr and 2 atm, following the procedure described in the '933 application.
- 16. In accordance with the procedure described in the '933 application, Dr. Terrones collected 1 gram of soot at the lower pressure by performing several runs at the lower pressure; about 100 mg. of soot, on average, was obtained from each run.
- 17. In an effort to meet the time schedule imposed by the United States Patent and Trademark Office described above, Dr. Terrones did not attempt to collect one gram of soot at

the higher pressure, but instead chose to separate the fullerenes that were produced from a run conducted at 2 atm.

- 18. To economize the time, and to meet the deadline imposed by the United States
  Patent Office, I did not have Dr. Terrones separate the fullerenes from the soot. I decided to
  have the soot produced by Dr. Terrones at the lower pressure forwarded to my colleague,
  Professor Adam Darwish, at Sussex University, for the separation of fullerenes from the soot. In
  this way, there would be a minimum loss of time, as Dr. Darwish would be isolating fullerenes
  from the soot, while Dr. Terrones was effecting the vaporization of graphite at the higher
  pressure.
- 19. Dr. Darwish utilized standard chemical techniques to separate the  $C_{60}$ ,  $C_{70}$  and the other fullerenes from the soot, described in the '933 application and/or known and routine to one of ordinary skill in the art in September 1990. Specifically, Dr. Darwish used soxhlet extraction and preparative HPLC, which are techniques which were known and routine to one of ordinary skill in the art in September 1990.
- 20. From the 1g sample of soot produced at 100 torr, Dr. Darwish collected 65 mg of  $C_{60}$ , crystals, 15 mg of  $C_{70}$  and 1-5 mg of the higher fullerenes (i.e., fullerenes other than  $C_{60}$  and  $C_{70}$ ). Mass spectra data confirmed the products produced. The  $C_{60}$ ,  $C_{70}$ , and the total amount of the higher fullerenes obtained from the soot produced from the vaporization of graphite at 100 torr, in accordance with the procedure described in the '933 application were produced in macroscopic amounts.
- 21. Attached hereto as Exhibit 4 is evidence of the  $C_{60}$  produced at the lower pressure from the vaporization of graphite in the bell jar apparatus at the lower pressure, produced in accordance with the procedure described in the '933 application. Exhibit 4(a) is the mass

spectrum of the  $C_{60}$ , which verifies that the product is  $C_{60}$ . Moreover, the clean spectra as well as the HPLC tracing in Exhibit 4(b) show that the  $C_{60}$  produced is relatively pure. Exhibit 4(c) is a photograph of a sample of  $C_{60}$  dissolved in toluene, and Exhibit 4(d) is a photograph of the crystals of  $C_{60}$  produced at the lower pressure after evaporation of the toluene. As shown in Exhibit 4(d), the  $C_{60}$  produced at the lower pressure was present in macroscopic amounts. In fact, 65 mg of the  $C_{60}$  product, which was isolated from the soot produced from the vaporization of graphite at 100 torr, can easily be seen with the naked eye.

- 22. Attached hereto as Exhibit 5 is evidence of the C<sub>70</sub> isolated from the soot at the lower pressure from the vaporization of graphite, produced in accordance with the procedure described in the '933 application. Exhibit 5(a) is the mass spectrum of the C<sub>70</sub> isolated from the soot produced from the graphite at 100 torr, confirming that the product produced is C<sub>70</sub>. Moreover, the mass spectrum as well as the HPLC tracing in Exhibit 5(b) show that the C<sub>70</sub> produced is relatively pure. Exhibit 5(c) is a photograph of a sample of C<sub>70</sub> dissolved in toluene and Exhibit 5(d) is a photograph of a sample of the crystals of C<sub>70</sub> produced at the lower pressure after evaporation of toluene. As shown by Exhibit 5(d), the C<sub>70</sub> produced at the lower pressure was present in macroscopic amounts. In fact, 15 mg of product, which is the amount of C<sub>70</sub> produced from the soot produced from the vaporization of graphite at 100 torr, can easily be seen with the naked eye.
- 23. The amount of the higher fullerenes (i.e. fullerenes other than  $C_{60}$  and  $C_{70}$ ) collected in total from the soot prepared from the vaporization of graphite at the lower pressure, in accordance with the procedure described in the '933 application, was also produced in macroscopic amounts; 7 mg of the higher fullerenes, which were collected from the soot produced from the vaporization of graphite at 100 torr, also can be seen with the naked eye.

From the data, the following fullerenes were also isolated from the vaporization at the lower pressure, the identities of which were confirmed by mass spectra:  $C_{70}O$ ,  $C_{76}$ ,  $C_{78}$ ,  $C_{84}$ ,  $C_{86}$ , and  $C_{90}$ .

- 24. Reference is made to Exhibit 6. The upper portion depicts photographs of samples of each of the fullerenes discussed in the previous paragraph dissolved in toluene together with photographs of the crystals formed from evaporation of exactly the half volume of the toluene solution obtained, except for C<sub>86</sub>, where all the toluene solution was evaporated to dryness, while the lower photographs show crystals of each of the fullerenes discussed in Paragraph 24 obtained from the evaporation of toluene. As evidenced by the photographs of the crystals of each of these fullerene products identified in the previous paragraphs, these crystals were seen with the naked eye.
- 25. Dr. Darwish also separated  $C_{60}$ ,  $C_{70}$  and higher fullerenes from the 100-mg. sample produced by Professor Terrones when the vaporization was conducted at the higher pressure of 2 atm. using a current of 100 amps, following the procedure described in the '933 application. The discussion in paragraphs 27-31 relates to the results of this experiment.
- 26. From the 100 mg sample produced at 2 atm and 100 amps, Dr. Darwish obtained 9 mg or 9% yield of fullerenes. He isolated 5.0 mg of  $C_{60}$  crystals, 1.5 mg of  $C_{70}$  crystals and 1.0 mg of higher fullerenes from the soot.
- 27. The mass spectrum of the  $C_{60}$  sample produced at 2 atm is depicted in Exhibit 7, confirming that  $C_{60}$  was produced and was relatively pure. A sample was dissolved in toluene, and when the toluene was evaporated,  $C_{60}$  crystals were collected. Exhibit 7 also includes a photograph of the  $C_{60}$  dissolved in the toluene solution and a photograph of the  $C_{60}$  crystals obtained from the evaporation of toluene. Thus, as shown by the photograph of the  $C_{60}$  crystals

in Exhibit 7,  $C_{60}$  was isolated in macroscopic amounts from the 100 mg sample of soot produced by Dr. Terrones from the vaporization of graphite at the higher pressure, prepared in accordance with the procedure described in the '933 application.

- 28. The mass spectrum of the  $C_{70}$  sample produced at 2 atm is depicted in Exhibit 8, confirming that the  $C_{70}$  that was produced was relatively pure. A sample of the  $C_{70}$  was dissolved in toluene and when the toluene was evaporated,  $C_{70}$  crystals were produced. Figure 8 also includes a photograph of a sample of  $C_{70}$  solution in toluene and a photograph of the  $C_{70}$  crystals produced after evaporation of the toluene. Thus, as shown by the photograph in Exhibit 8, the  $C_{70}$  crystals can be seen with the naked eye. Thus,  $C_{70}$  was isolated in macroscopic amounts from the 100 mg sample of soot produced from the vaporization of graphite at 2 atm, prepared in accordance with the procedure described in the '933 application.
- 29. Besides C<sub>60</sub> and C<sub>70</sub>, higher fullerenes ("HFs") were produced. In fact, the mass spectrum provides evidence that higher fullerenes up to C<sub>104</sub> were produced at the higher pressure. A copy of the mass spectrum is attached hereto as Exhibit 9. A sample of the higher fullerenes, obtained from the 100 mg sample of soot that was obtained from the vaporization of soot at 2 atm, was dissolved in toluene and when the toluene was evaporated, crystals of the higher fullerenes were produced. Exhibit 9 also includes a photograph of a sample of the higher fullerenes dissolved in toluene and a photograph of the solid crystals that were formed after evaporation of the solvent. The photograph shows crystals of higher fullerenes that can be seen with the naked eye. Thus, macroscopic amounts of the higher fullerenes were obtained from the vaporization of graphite at 2 atm, prepared in accordance with the procedure described in the '933 application.

- 30. Exhibit 10 depicts the photographs of  $C_{60}$ ,  $C_{70}$  and the higher fullerenes in solution in toluene that were isolated from the 100 mg sample of soot produced from the vaporization of graphite at 2 atm pressure, prepared in accordance with the procedure described in the '933 application and the photographs of crystals of  $C_{60}$ ,  $C_{70}$  and the higher fullerenes that were obtained after evaporation of the toluene. Inasmuch as the crystals of  $C_{60}$ ,  $C_{70}$ , and the higher fullerenes were visible, as evidenced by the photographs in Exhibit 10, the  $C_{60}$ ,  $C_{70}$  and higher fullerenes were produced in macroscopic amounts from the vaporization of graphite at the higher pressure, prepared in accordance with the procedure described in the '933 application.
- 31. It is observed that the bell jar apparatus and the aluminum reactor were both limited by the constraint that only permitted the vaporization to be conducted for a limited time before the vaporization had to be stopped. Nevertheless, even with this constraint, in the present circumstances, the process described in the '933 application produced macroscopic amounts of  $C_{60}$ ,  $C_{70}$  and higher fullerenes when the process was conducted at both the lower pressures of 100 torr and at the higher pressure of 2 atm.
- 32. As shown by the data produced by the experiments conducted in accordance with the process described in the '933 application, as described herein,  $C_{60}$  and  $C_{70}$  and other fullerenes produced were obtained in amounts that could be seen with the naked eye. The  $C_{60}$ ,  $C_{70}$  and the higher fullerenes were produced in macroscopic amounts. See Exhibits 4-10.
- 33. Thus, by following the procedure described in the '933 application, the evidence provided herein shows that the process described in the application produces several species of fullerenes, including  $C_{60}$ ,  $C_{70}$  and higher fullerenes in macroscopic amounts, both at the lower pressure, i.e., 100 torr, and at the higher pressure, 2 atm.

- 34. Moreover, the results described hereinabove show that a high yield of fullerenes is recovered from the soot prepared in accordance with the procedure described in the '933 application; approximately 10% of the soot was comprised of fullerenes. This is still among the highest yield of fullerenes obtained from soot to date. From the mass spectrum, it is evident that fullerenes other than those characterized herein were present in the soot, macroscopic amounts of these other fullerenes may be isolated if additional runs were performed.
- 35. The soot was prepared by Dr. Terrones merely following the procedure described in the '933 application, especially Examples 1 and 2; there was no undue amount of experimentation in the preparation thereof. Further, the separation of macroscopic amounts of fullerenes including C<sub>60</sub> and C<sub>70</sub> from the soot was routine to one of ordinary skill in the art on August 30, 1990. Thus, the process described in the '933 application is sufficiently detailed for the skilled artisan on August 30, 1990 to prepare macroscopic amounts of C<sub>60</sub> and C<sub>70</sub>, without undue experimentation.
- 36. The realization by Huffman and Kratschmer of macroscopic quantities of fullerene, e.g.,  $C_{60}$  and  $C_{70}$  and the isolation and characterization of same, e.g.,  $C_{60}$  and  $C_{70}$  by the methods described in the '933 application are recognized by the knowledgeable scientific community as a long awaited and much needed breakthrough; it was surprising that relatively high yields of fullerenes, such as  $C_{60}$ , could be achieved by these methods. The difficulties that existed in the quest for  $C_{60}$  are well elaborated in the article entitled "Fullerenes" by Robert F. Curl and Richard E. Smalley, printed in <u>Scientific American</u>, Oct. 1991, pp. 54-62 attached hereto as Exhibit 11.
- 37. Although the discovery described in the Huffman and Kratschmer application may seem simplistic to the uninformed, especially in hindsight, their discovery was quite

remarkable. The Kratschmer and Huffman method described in the '933 application is all the more remarkable for the fact that so simple a procedure so readily produces large amounts of fullerenes. This is readily appreciated if one considers the historical perspective. Even since the detection of C<sub>60</sub> by the collaborative efforts of the Smalley and Kroto groups in 1985, as described in the article in Nature, 1985, 318, 162-163, attached hereto as Exhibit 12, experts, such as Drs. Smalley and myself, both together and separately worked to prepare fullerenes on a larger scale. For five long years, many attempts were tried, but each was unsuccessful. Finally, to my expert knowledge, one group, Huffman and Kratschmer, was the first to find and publish a methodology capable of producing and isolating fullerenes, such as C<sub>60</sub>, in macroscopic amounts. This methodology is described in the '933 application and satisfied a long felt need in this area.

38. The scientific community has unanimously and unequivocally acknowledged and recognized that Kratschmer and Huffman were the first to have developed a process for preparing and isolating fullerenes, e.g.,  $C_{60}$ , in macroscopic amounts, and were the first to isolate the fullerenes, e.g.,  $C_{60}$ , in macroscopic amounts and in consequence thereof has presented them with several awards. Even the press release by the Royal Swedish Academy of Sciences regarding the Nobel Prize in Chemistry in 1996, attached hereto as Exhibit 13, recognized the contribution of Huffman and Kratschmer by acknowledging that these two scientists for the first time produced "isolable quantities of  $C_{60}$ ". (See Page 2 of Exhibit 13). As stated in the press release:

[t]hey obtained a mixture of  $C_{60}$  and  $C_{70}$  the structures of which could be determined...The way was thus open for studying the chemical properties of  $C_{60}$  and other carbon clusters such as  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$  and  $C_{84}$ ...An entirely new branch of chemistry developed with consequences in such diverse areas as

astrochemistry, superconductivity and materials chemistry/physics.

- 39. Thus, in my opinion, the '933 application describes a process for preparing fullerenes, including  $C_{60}$ , in macroscopic amounts and the process described therein provides sufficient detail for an ordinary skilled artisan in August 1990 to make the same in the absence of undue amount of experimentation.
- 40. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: ˈ

Harold W. Kroto, Ph.D.

#### Professor Sir Harold Kroto FRS

Born 1939 Wisbech Cambridgeshire, educated Bolton School. BSc (First class honours degree Chemistry, 1961) and a PhD (Molecular Spectroscopy, 1964) University of Sheffield. Postdoctoral work at the National Research Council (Ottawa, Canada 1964-66) and Bell Telephone Laboratories (Murray Hill, NJ USA 1966-67); Tutorial Fellow 1967, lecturer 1968, Reader 1977University of Sussex (Brighton) in 1967. He became a professor in 1985 and a Royal Society Research Professor in 1991. In 1996 he was knighted for his contributions to chemistry and later that year, together with Robert Curl and Richard Smalley (of Rice University, Houston, Texas), received the Nobel Prize for Chemistry for the discovery of C60 Buckminsterfullerene a new form of carbon.

#### Research fields cover several major topics:

- (1961-1970) Electronic spectroscopy of free radicals and unstable intermediates in the gas phase, ii) Raman spectroscopy of intermolecular interactions in the liquid phase and iii) Theoretical studies of electronic properties ground and excited states of small molecules and free radicals.
- 2) (1970-1980) Research focused on the creation of new molecules with multiple bonds between carbon and elements, mainly of the second and third row of the Periodic Table (S, Se and P), which were reluctant to form such a link. These studies showed that many of these previously assumed impossible species could be produced, studied by spectroscopy and used as valuable synthons leading to a wide class of new phosphorus containing compounds. In particular the spectroscopic studies of molecules with carbon-phosphorus multiple bonds (C=P and C=P) were the pioneering studies that initiated the now prolific field of Phosphaalkene/alkyne Chemistry.
- 3) (1975-1980) Laboratory and radioastronomy studies on long linear carbon chain molecules (the cyanopolyynes) led to the surprising discovery (by radioastronomy) that they existed in interstellar space and also in stars. Since these first observations the carbon chains have become a major area of modern research by molecular spectroscopists and astronomers interested in the chemistry of space.
- 4) (1985-1990) The revelation (1975-1980) that long chain molecules existed in space could not be explained by the then accepted ideas on interstellar chemistry and it was during attempts to rationalise their abundance that C<sub>60</sub> Buckminsterfullerene was discovered. Laboratory experiments at Rice University, which simulated the chemical reactions in the atmospheres of red giant carbon stars, serendipitously revealed the fact that the C<sub>60</sub> molecule could self-assemble. This ability to self-assemble has completely changed our perspective on the nanoscale behaviour of graphite in particular and sheet materials in general. The molecule was subsequently isolated independently at Sussex and structurally characterised.
- 5) (1990-) Present research focuses on Fullerene chemistry and the nanoscale structure of new materials, in particular nanotubes. This has led to a wide range of new nanostructured materials the first insulated nanowires and new perspectives on the mechanism of nanotube formation.

Key collaborations: With D R M Walton (Sussex), T Oka, L Avery, N Broten and J MacLeod (NRC Ottawa) on carbon chain molecules in the laboratory and space; J F Nixon on phosphaalkene/alkyne chemistry (at Sussex); with J P Hare, P R Birkett, A Darwish, M Terrones, W K Hsu, N Grobert, Y Q Zhu, R Taylor and D R M Walton on Fullerene chemistry and nanostructures (at Sussex); with R F Curl, J R Heath, S C O'Brien, Y Liu and R E Smalley (at Rice University Texas) on the discovery of Buckminsterfullerene.

**Education:** Chairman of the board of the Vega Science Trust which is produces science programmes for network television. 75 have been made and so far 55 have been broadcast on the BBC Learning Zone educational slot. Member of National Advisory Committee on Cultural and Creative Education.

Scientific Awards etc: Tilden Lectureship of the RSC (1981); International Prize for New Materials by the American Physical Society (shared 1992 with Robert Curl and Richard Smalley); Italgas Prize for Innovation in Chemistry (1992); Royal Society of Chemistry Longstaff Medal (1993); Hewlett Packard Europhysics Prize (shared with Wolfgang Kraetschmer, Don Huffman and Richard Smalley 1994);

Nobel Prize for Chemistry in 1996 (shared with Robert Curl and Richard Smalley); American Carbon Society Medal for Achievement in Carbon Science (shared with Robert Curl and Richard Smalley1997); Blackett Lecturship 1999 (Royal Society); Faraday Award and Lecture 2001 (Royal Society). Dalton Medal 1998 (Manchester Lit and Phil), Erasmus Medal of Academia Europaea, Ioannes Marcus Marci Medal 2000 (Prague) for contributions to molecular spectroscopy.

Fellowships etc: Fellow of the Royal Society (1990), Fellow of the Royal Society of Chemistry; President of the Royal Society of Chemistry (2002-2004), Mexican Academy of Science; Member Academia Europaea (1993); Hon. Foreign Member Korean Academy of Science and Technology (KAST) (1997); Hon. Fellow of the Royal Microscopical Society (1998); Hon. Fellow of the Royal Society of Edinburgh (1998); Hon Fellow of the RSC (2000).

Honorary degrees: Université Libre (Bruxelles), Stockholm (Sweden), Limburg (Belgium), Sheffield, Kingston, Sussex, Helsinki (Finland), Nottingham, Yokohama City (Japan), Sheffield-Hallam, Aberdeen, Leicester, Aveiro (Portugal), Bielefeld Germany), Hull, Manchester Metropolitan, Exeter, Hong Kong City (China), Gustavus Adolphus College (Minnesota, USA), University College London, Patras (Greece), Halifax (NovaScotia, Canada), Strathclyde; Hon Fellowship: Bolton Institute.

Graphic design work has resulted in numerous posters, letterheads, logos, book/journal covers, medal design etc. Awards: Sunday Times Book Jacket Design competition (1964) and more recently the Moet Hennessy/Louis Vuitton Science pour l'Art Prize (1994). Citation in the international design annual "Modern Publicity" (1979) for the cover of "Chemistry at Sussex"

**TV/Internet Science Programmes**: Prix Leonardo Bronze Medal (2001); Chemical Industries Association (Presidents prize short list1998 and 1999)



# Harry Kroto's Curriculum Vitae

# Part B - Harry's main research intrests and research highlights

#### Main research areas:

- I Spectroscopy of Unstable Species and Reaction Intermediates (Infrared, Photoelectron, Microwave and Mass Spectrometry)
- II Astrophysics (Interstellar Molecules and Circumstellar Dust)
- III Cluster Science (Carbon and Metal Clusters, Microparticles, Nanofibres)
- IV Fullerene Chemistry, Nanoscience and Nanotechnology

# Research Highlights (Ref Nos - Key Refs List)

- a) First detection of  $^{1}\Delta$  state of a polyatomic free radical (NCN by flash photolysis) [3,4]
- b) Theoretical studies of ground and electronically excited sates of small molecules [5,6]
- c) Detection of liquid phase intermolecular interactions using Raman Spectroscopy [ 7-10]
- d) Breakthrough in the detection of new unstable species (thioaldehydes, thiocarbonyls thioborines) using combination of microwave and photoelectron spectroscopy techniques [12,15,18-22,31,80]
- e) Synthesis in 1976 of the first phoaphaalkenes (compounds containing the free carbon phosphorus double bond) in particular CH2=PH (with N P C Simmons and J F Nixon, Sussex), [28, 80]
- f) Monograph "Molecular Rotation Spectra" [23]
- g) Synthesis in 1976 of the first analogues of HCP, the phosphaalkynes which contain the carbon phoshorus triple bond - in particular CH3CP (with N P C Simmons and J F Nixon, Sussex), [29,80]
- h) The discovery (1976-8) of the cyanopolyynes, HCnN (n=5,7,9), in interstellar space (with D R M Walton A J Alexander and C Kirby (Sussex) and T Oka, L W Avery, N W Broten and J M MacLeod (NRC Ottawa)), Ref 4-6, based on microwave measurements made at Sussex, [27,30,35,80]
- The discovery of C60: Buckminsterfullerene in 1985 (with J R Heath, S C O'Brien, R F Curl and R E Smalley), [100,112,139,239]
- j) The detection of endohedral metallofullerene complexes (with J R Heath, S C O'Brien, Q Zhang, Y Liu, R F Curl, F K Tittel and R E Smalley), [101,139]

- k) The prediction that C60 should be produced in combustion processes and might indicate how soot is formed (with Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl and R E Smalley) [103,139]
- The explanation of why C70 is the second stable fullerene (after C60) and the discovery of the Pentagon Isolation Rule as a criterion for fullerene stability in general [107,112,139,239]
- m) The prediction of the tetrahedral structure of C28 and the possible stability of "tetravalent" derivatives such as C28H4 [107,112,139,239]
- The prediction that giant fullerenes have quasi-icosahedral shapes and the detailed structure of concentric shell graphite microparticles (with K G McKay), [111,112,139,239]
- The mass spectrometric identification and solvent extraction (with J P Hare and A Abdul-Sada) of C60 from arc processed carbon in 1990 independently from and simultaneously with the Heidelberg/Tucson group; Refs [121,239]
- p) The chromatographic separation/purification of C60 and C70 and 13C NMR measurements which provided unequivocal proof that these species had fullerene cage structures (with J P Hare and R Taylor, Sussex), Refs [121,139,239]
- q) Crystal structure of C60 [135,138]
- r) Main Fullerene chemistry breakthroughs: C60(ferrocene)2 [162], characterisation of C60Hal6 [174,149], C60(P4)2 [187], [192]
- s) Nanoscience and Nanotechnology advances: Condensed phase nanotubes [205], nanoscale BN structures [224], partly alignednanotube bundles [233], nanotube formation mechanisms [161,238], silicon oxide nanostructures [247], Si surface-deposited fullererene studies [251], insulated carbon nanotube conductors [297]

NB General review refs underlined

Website Created And Maintained By: Christopher Dean This Page Last Updated 15/02/2003



Publications: 1963 To 2002

As the publication list is large It has been broken down chronologically into four parts

The first part 1963 - 1984, is contained on this page, if however you are looking for information on other years please click one of the following links:

Years: 1963 - 1984 1985 - 1993 1994 - 2000 2001 - 2002

- 1 R N Dixon and H W Kroto, 'High resolution study of the spectrum of the CBr radical', Trans Faraday Soc, 59, 1484-1489 (1963).
- 2 R N Dixon and H W Kroto, 'The electronic spectrum of nitrosomethane, CH3NO', EE Proc. Roy. Soc., 283, 423-432 (1965).
- 3 H W Kroto, 'Singlet and triplet states of NCN in the flash photolysis of cyanogen azide', ∴ J. Chem. Phys., 44, 831-832 (1966).
- 4 H W Kroto, The 1 u 1 g electronic spectrum of NCN, Can. J. Phys., 45, 1439-1450 (1967).
- 5 H W Kroto and D P Santry, 'CNDO molecular-orbital theory of molecular structure. I. The virtual-orbital approximation to excited states', J. Chem. Phys., 47, 792-797 (1967).
- 6 H W Kroto and D P Santry, 'Semiempirical molecular-orbital spectra. U II. L Approximate open-shell theory', J. Chem. Phys., 47, 2736-2743 (1967).
- 7 H W Kroto and Y-H Pao, 'Effect of intermolecular interactions on line shapes and depolarization factors of highly polarized Raman lines', J. Optical Society of America, 58, 479-483 (1968).
- 8 H J Clase and H W Kroto, 'The effect of intermolecular interactions on the isotope structures of the Raman bands of CHCl3 , CCl3F and CCl3CN', Mol. Phys., 15, 167-172 (1968).
- 9 PR Carey, HW Kroto and MA Turpin, 'Chlorine isotope effects on the 19F resonance of CCI3F and the use of this signal as a reference in high-resolution nuclear magnetic resonance', Chem. Comm., 1188 (1969).
- 10 H W Kroto and J J C Teixeira-Diaz, 'Theory of the effect of intermolecular interactions on the Raman spectra of liquid CHCl3L and CFCl3', Mol. Phys., 16, 773-782 (1970).
- 11 H W Kroto, T F Morgan and H H Sheena, 'Flash photolysis of cyanogen azide, NCN3', Trans. Faraday Soc., 66, 2237-2243 (1970).
- 12 G H King, H W Kroto and R J Suffolk, 'The photo-electron spectrum of a short-lived species in the decomposition products of CS2', Chem. Phys. Letts., 13, 457-458 (1972).

- 13 J P Jesson, H W Kroto and D A Ramsay, 'Quasiplanarity of pyridine in its first excited singlet state', J. Chem. Phys., 56, 6257-6258 (1972).
- 14 H W Kroto and J J C Teixeira-Dias, 'The effects of intermolecular interactions in the Raman spectrum of liquid CS2', Spectrochim. Acta., 28A, 1497-1502 (1972).
- 15 H W Kroto and R J Suffolk, 'The photoelectron spectrum of an unstable species in the pyrolysis products of dimethyldisulphide', Chem. Phys. Letts., 15, 545-548 (1972).
- 16 C C Costain and H W Kroto, 'Microwave spectrum, structure and dipole moment of cyanogen azide, NCN3', Can. J. Phys., 50, 1453-1457 (1972).
- 17 A J Careless, M C Green and H W Kroto, 'The microwave spectrum of trimethylsilyl isocyanate (CH3)3SiNCO', Chem. Phys. Letts., 16, 414-418 (1972).
- 18 H W Kroto and R J Suffolk, 'The photoelectron spectrum of F2CS and fluorine substitution shifts', Chem. Phys. Letts., 17, 213-216 (1972).
- 19 A J Careless, H W Kroto and B M Landsberg, 'The microwave spectrum, structure and dipole moment of thiocarbonyl fluoride, F2CS', Chem. Phys., 1, 371-375 (1973).
- 20 H W Kroto, R J Suffolk and N P C Westwood, 'The photo-electron spectrum of thioborine, HBS', Chem. Phys. Letts., 22, 495-498 (1973).
- 21 K Georgiou, H W Kroto and B M Landsberg, 'Microwave spectrum of thioketene, H2C=C=S', Chem. Commun., p739-740 (1974).
- 22 H W Kroto, B M Landsberg, R J Suffolk and A Vodden, 'The photoelectron and microwave spectra of the unstable species thioacetaldehyde, CH3CHS, and thioacetone, (CH3)2CS', Chem. Phys. Letts., 29, 265-269 (1974).
- 23 H W Kroto, 'Molecular Rotation Spectra', (monograph, pp311) John Wiley, London (1975).
- A J Careless and H W Kroto, 'Rotational transitions in degenerate vibrational states of C3v symmetric top molecules with application to CH3CN',J. Mol. Spectrosc., 57, 189-197 (1975).
- 25 A J Careless and H W Kroto, 'Analysis of the microwave rotation spectrum of silyl cyanide, SiH3CN in its ground and vibrationally excited states', J. Mol. Spectrosc., 57, 198-214 (1975).
- 26 H W Kroto, M F Lappert, M Maier, J B Pedley, M Vidal and M F Guest, 'The Hel photoelectron spectra of mixed boron trihalides and the microwave spectrum of BCIF2', Chem. Commun., 810-812 (1975).
- 27 L W Avery, N W Broten, J M MacLeod, T Oka and H W Kroto, 'Detection of the heavy interstellar molecule cyanodiacetylene', Astrophys. J., 205, L173-175 (1976).
- 28 M J Hopkinson, H W Kroto, J F Nixon and N P C Simmons, 'The detection of unstable molecules by microwave spectroscopy: phospha-alkenes CF2=PH, CH2=PCI and CH2=PH', J.C.S. Chem. Comm., 513-515 (1976).
- 29 M J Hopkinson, H W Kroto, J F Nixon and N P C Simmons, 'The detection of the reactive molecule 1-phosphapropyne, CH3CL P, by microwave spectroscopy', Chem. Phys. Letts., 42, 460-461 (1976).

- 30 A J Alexander, H W Kroto and D R M Walton, 'The microwave spectrum, substitution structure and dipole moment of cyanobutadiyne, HC5N', J. Mol. Spectrosc., 62, 175-180 (1976).
- 31 H W Kroto and B M Landsberg, 'The Microwave Spectrum, Substitution Structure, Internal Rotation Barrier and Dipole Moment of Thioacetaldehyde, CH3CHS', J. Mol. Spectrosc., 62, 346-363 (1976).
- 32 H W Kroto and M Maier, 'The Microwave Spectrum, Structure and Quadrupole Coupling Constants of Boronchloridedifluoride, BCIF2', J. Mol. Spectrosc., 65, 280-288 (1977).
- 33 D C Frost, H W Kroto, C A McDowell and N P C Westwood, 'The Hel Photoelectron Spectra of the Isoelectronic Molecules, Cyanogenazide NCN3 and Cyanogen isocyanate NCNCO', J. Electron Spectrosc., 11, 147-156 (1977).
- 34 J N Murrell, H W Kroto and M F Guest, 'Double-bonded divalent silicon', J.C.S. Chem. Comm., 619-620 (1977).
- 35 H W Kroto, C Kirby, D R M Walton, L W Avery, N W Broten, J M MacLeod and T Oka, The Detection of Cyanohexatriyne, HC7N, in Heiles' Cloud 2', Astrophysics J., 219, L133-L137 (1978).
- 36 H W Kroto, J N Murrell, A Al-Derzi and M F Guest, 'Calculated Structures and Microwave Frequencies of HNSi and HSiN, Astrophysical J., 219, 886-890 (1978).
- 37 C Kirby and H W Kroto, 'Microwave and Photoelectron Study of cis- and trans-Isocyanatoethene CH2=CHNCO (vinylisocyanate)', J. Mol. Spectrosc., 70, 216-228 (1978).
- 38 M Hutchinson and H W Kroto, 'The Microwave Spectrum, Structure and Barrier to Internal Rotation of Selenoacetaldehyde, CH3CHSe', J. Mol. Spectrosc., 70, 347-356 (1978).
- 39 H W Kroto, J F Nixon, N P C Simmons and N P C Westwood, 'FCLP, 1-Fluorophosphaethyne: Preparation and Detection by Photoelectron and Microwave Spectroscopy', J. Am. Chem. Soc., 100, 446-448 (1978).
- 40 A J Alexander, H W Kroto, M Maier and D R M Walton, 'The Microwave Spectra of Symmetric Top Polyacetylenes: 1,3,5-Heptatriyne CH3C6H and 1-Cyano-2,4-Pentadiyne CH3C4CN', J. Mol. Spectrosc., 70, 84-90 (1978).
- 41 C Kirby, H W Kroto and N P C Westwood, 'The Detection of Chlorothioborine, CIBS, a New Unstable Triatomic Molecule by Photoelectron and Microwave Spectroscopy', J. Am. Chem. Soc., 100, 3766-3768 (1978).
- 42 C Kirby, H W Kroto and M J Taylor, 'The Detection of the New Reactive Molecule Methyl(sulphido)boron CH3BS, by Microwave Spectroscopy', J.C.S. Chem. Comm., 19-20 (1978).
- 43 N W Broten, T Oka, L W Avery, J M MacLeod and H W Kroto, 'The Detection of HC9N in Interstellar Space', Astrophys. J., 223, L105-107 (1978).
- 44 H W Kroto, 'Chemistry between the Stars', New Scientist 79, 400-403 (1978); [No.1115, 10 Aug.].
- 45 K Georgiou, B M Landsberg and H W Kroto, 'The Microwave Spectrum Structure and

- Dipole Moment of Thioketene CH2=C=S', J. Mol. Spectrosc., 77, 365-373 (1979).
- 46 N P C Westwood, H W Kroto, J F Nixon and N P C Simmons, 'Formation of 1-Phosphapropyne CH3CP by Pyrolysis of Ethyl Dichlorophosphine: a He(I) Photoelectron Spectroscopic Study', J.C.S. Dalton, 1405-1408 (1979).
- 47 H W Kroto, J F Nixon and N P C Simmons, 'The Microwave Spectrum of 1-Phosphapropyne, CH3CLP: Molecular Structure, Dipole Moment and Vibration Rotation Analysis', J. Mol. Spectrosc., 77, 270-285 (1979).
- 48 H E Hosseini, J F Nixon, H W Kroto, S Brownstein, J R Morton and K F Preston, '

  19F and 31P NMR characterisation of Phospha-alkene and Phospha-alkyne Intermediates in the Hydrolysis of Perfluoroalkyl-phosphines', J.C.S. Chem. Comm., 653-654 (1979).
- 49 H E Hosseini, H W Kroto, J F Nixon, O Ohashi, '19F and 31P NMR Characterisation of the Phosphaalkene CF3P=CF2, Intermediates in the alkaline hydrolysis of Bis (trifluoromethyl) phosphine', J. Organometallic Chem., 181, C1-C3 (1979).
- 50 H W Kroto, 'The Detection of Unstable Species using Microwave, Photoelectron and Radioastronomy Techniques', 14th International Symposium on Free Radicals, Sanda, Japan., 147-156 (1979).
- 51 T Cooper, H W Kroto, J F Nixon and O Ohashi, 'The Detection of C-Cyanophosphaethyne NCCP, by Microwave Spectroscopy', J. Chem. Soc. Chem. Comm., 333-334 (1980).
- 52 H W Kroto, J F Nixon and N P C Simmons, 'Microwave Spectrum, Structure, Dipole Moment and Vibrational Satellites of FCP', J. Mol. Spectrosc. 82, 185-192 (1980).
- 53 M Hutchinson, H W Kroto and D R M Walton, 'Rotation-Vibration Analysis of the Microwave Spectrum of Cyanobutadiyne, HC5N', J. Mol. Spectrosc., 82, 394-410 (1980).
- 54 C Kirby and H W Kroto, 'The Microwave Spectrum of Methyl-Sulphido-Boron, CH3B=S: Substitution Structure, Dipole Moment and Vibration-Rotation Analysis', J. Mol. Spectrosc., 83, 1-14 (1980).
- 55 K Georgiou and H W Kroto, 'The Microwave Spectrum Structure and Dipole Moment of Trans 2-Propenethial (Trans-thioacrolein), CH2=CHCH=S, J. Mol. Spectrosc., 83, 94-104 (1980).
- 56 C Kirby and H W Kroto, 'The Microwave Spectrum of Chloro-Sulphido-Boron CIB=S: Molecular Structure, Dipole Moment, Quadrupole Moment and Vibration-Rotation Analysis', J. Mol. Spectrosc., 83, 130-147 (1980).
- 57 C Kirby, H W Kroto and D R M Walton, 'The Microwave Spectrum of Cyanohexatriyne, HC7N', J. Mol. Spectrosc., 83, 261-265 (1980).
- 58 M King and H W Kroto, 'Microwave Study of the Thermal Isomerisation of Sulphurdicyanide, S(CN)2 to Cyano-isothiocyanate, NCNCS, J. Chem. Soc. Chem. Comm., 606 (1980).
- 59 H W Kroto, J F Nixon, K Ohno and N P C Simmons, 'The Microwave Spectrum of Phosphaethene, CH2=PH', J. Chem. Soc. Chem. Comm., 709 (1980).
- 60 H W Kroto, C Kirby, D R M Walton, L W Avery, N W Broten, J M McLeod and T Oka, 'Detection of a Complex New Interstellar Species with a Molecular Weight of 99', in Les

- Spectres des Molecules Simples Au Laboratoire et en Astro-Physique, XXI Colloque Int. Astr. 1977, 83-86 (1980).
- 61 H W Kroto, 'The Detection of Unstable Species Using Microwave Photoelectron and Radioastronomy Techniques', Chimia, 34, 313 (1980).
- 62 H Eshtiagh-Hosseini, H W Kroto, J F Nixon, M L Maah and M J Taylor, 'Synthesis of Phospha-alkene Transition Metal Complexes', J.C.S. Chem. Comm., 199-200 (1981).
- 63 T A Cooper, M A King, H W Kroto and R J Suffolk, 'The Detection of Unstable Monomeric Selenidoborons: Chloroselenidoboron CIB=Se', J.C.S. Chem. Comm., 353-354 (1981).
- 64 M A King, H W Kroto, J F Nixon, D Klapstein, J P Maier and O Marthaler, 'Emission Spectra of the Phosphaethyne Cations, HCP+ and DCP+', Chem. Phys. Letts., 82, 543 (1981).
- 65 H W Kroto and J F Nixon, 'Phosphaalkenes, R2C=PR and Phosphaalkynes, RCP', A C S Symposium Series 171 (ed. L D Quin and J Verkade) No.79, 383-390, J Am. Chem. Soc.
- 66 J C T R Burckett-St.Laurent, P B Hitchcock, H W Kroto and J F Nixon, 'Novel Transition Metal Phosphaalkyne Complexes. X-Ray Crystal and Molecular Structure of a Side-bonded ButCP Complex of Zerovalent Platinum, Pt(PPh2)2(ButCP), J.C.S. Chem. Comm., 1141-1143 (1981).
- 67 H W Kroto, J F Nixon and K Ohno, 'The Microwave Spectrum, Structure and Dipole Moment of the Unstable Molecule Phosphaethene, CH2=PH',J. Mol. Spectrosc., 90, 367-373 (1981).
- 68 K Ohno, H W Kroto and J F Nixon, 'The Microwave Spectrum of 1-Phosphabut-1-yne-3-ene, CH2=CHCP', J. Mol. Spectrosc., 90, 507-511 (1981).
- 69 H W Kroto, J F Nixon and K Ohno, 'The Microwave Spectrum of Phosphabutadiyne, HCCCP', J. Mol. Spectrosc., 90, 512-516 (1981).
- 70 H W Kroto, 'The Spectra of Interstellar Molecules', International Reviews in Physical Chemistry, 1, 309-376 (1981).
- 71 J C T R Burckett-St.Laurent, H W Kroto, J F Nixon and K Ohno, 'The Microwave Spectrum of 1-Phenylphosphaethyne, C6H5CP', J. Mol. Spectrosc., 92, 158-161 (1982).
- 72 H W Kroto, 'Molecules in Space' Case Study 3 S247, Science Second Level Course, Open University 1981.
- 73 73 TEEDECHO H W Kroto, J F Nixon, M J Taylor, A A Frew and K W Muir, 'Synthesis and E NMR spectra of some platinum(II) complexes of the phospha-alkene, (mesityl) P=CPh2', Polyhedron, 1, 89-95 (1982).
- 74 J C T R Burckett-St.Laurent, T A Cooper, H W Kroto, J F Nixon, O Ohashi and K Ohno, 'The Detection of Some New Phospha-alkynes, RCP, using microwave spectroscopy', J. Mol. Struct., 79, 215 (1982).
- 75 M A King, D Klapstein, H W Kroto, J P Maier and J F Nixon, 'Emission spectra of the phosphaethyne cations of HCP+ and DCP+', J. Mol. Struct., 80, 23-28 (1982).
- 76 H W Kroto, 'Polyine im Universum', Nachr. Chem. Tech. Lab., 30, 765-770 (1982).

- 77 K Ohno, H Matsuura, H W Kroto and H Murata, 'Infra-red spectra of C-fluorophosphaethyne FCP and C-difluorophosphaethene CF2=PH', Chemistry Letters, 981-984 (1982).
- 78 H W Kroto, 'The interaction between chemistry and astronomy', in Submillimetre Wave Spectroscopy, J E Beckman and J P Phillips (eds.), Cambridge University Press, 203-217 (1982).
- 79 J C T R Burckett-St.Laurent, P B Hitchcock, H W Kroto, M F Meidine and J F Nixon, 'Novel transition metal phospha-alkyne complexes: tBuCP acting as 6 electron donor ligand. Synthesis, [C2(CO)6(mu-tBuCP)W(CO)5]', J. Organometallic Chem., 238, C82-C84 (1982).
- 80 H W Kroto, 'Semistable Molecules in the Laboratory and in Space', Royal Society of Chemistry Tilden Lecture; Chem. Soc. Revs., 11, 435-491 (1982).
- 81 J C T R Burckett-St.Laurent, M A King, H W Kroto, J F Nixon and R J Suffolk, 'Photoelectron Spectra of the Phospha-alkynes: 3,3-dimethyl-1-phosphabutyne, t-BuCP and 1-phenylphosphaethyne, PhCP', J.C.S. Dalton, 755 (1983).
- 82 S I Al-Resayes, S I Klein, H W Kroto, M F Meidine and J F Nixon, 'Synthesis of and Phospha-alkene-transition metal complexes and the first examples of complexes containing only ligated phospha-alkenes and phospha-alkynes', J.C.S. Chem. Comm., 930 (1983).
- 83 M A King, D Klapstein, H W Kroto, R Kuhn and J P Maier, 'The Spectroscopic Detection of the lons XBS+ and XCP+ (X=H, F, CI)', Bull. Soc. Chim. Belg., 92, 607 (1983).
- 84 84LIGELEGE K Ohno, H Matsuura, H Murata and H W Kroto, GE The Vibration-Rotation Spectrum of C-Fluorophoethyne FCP; Fermi Resonance and a Harmonic Force Field, J. Mol. Spectrosc., 100, 403-415 (1983).
- 85 J C T R Burckett-St.Laurent, P B Hitchcock, M A King, H W Kroto, M F Meidine, S I Klein, S I Al Resayes, R J Suffolk and J F Nixon, 'Synthesis, Structures and Photoelectron Spectra of Phospha-alkenes and Phospha-alkynes and their Transition Metal Complexes', Phosphorus and Sulphur, 18, 259-262 (1983).
- 86 H W Kroto, J F Nixon, O Ohashi and N P C Simmons, 'The Microwave Spectrum of 1-chloro-phosphaethene CH2=PCl', J. Mol. Spectrosc., 103, 113-124 (1984).
- 87 H W Kroto, 'Long Carbon Chains in Space', European Spectroscopy News, 53, 18-20 (1984).
- 88 T A Cooper, C Kirby, H W Kroto and P C Westwood, 'A Photoelectron Spectroscopic Study of the (FBS)n System (n=1-3)', J. Chem. Soc. Dalton Trans., 1047-1052 (1984).
- 89 H W Kroto, D McNaughton and O I Osman, 'The Detection of the New Molecule Prop-2-ynylidenamine, HC2CH=NH, by Microwave Spectroscopy', J. Chem. Soc. Chem. Comm., 993-994 (1984).
- 90 M A King, D Klapstein, H W Kroto, R Kuhn, J P Maier and J F Nixon, 'Emission Spectrum of the C-Fluorophosphaethyne Cation FCP+', J. Chem. Phys., 80(6), 2332-2335 (1984).
- 91 H W Kroto, 'A Discrepancy in the Fit between Bacterial and Interstellar Spectra', Observatory, 104, 135-136 (1984).

92 M A King and H W Kroto, 'He I Photoelectron Study of Cyanogen Isothiocyanate, NCNCS, Produced by Thermal Isomerization of Sulfur Dicyanide, S(CN)2', J. Am. Chem. Soc., 106, 7347-7351 (1984).

Website Created And Maintained By: Christopher Dean This Page Last Updated 23/02/2003



Publications: 1985 - 1993

Years: 1963 - 1984 1985 - 1993 1994 - 2000 2001 - 2002

- 93 H W Kroto, S I Klein, M F Meidine, J F Nixon, R K Harris, K J Packer and P Reams, '1-and 2-Coordination in Phospha-alkeneplatinum(0) Complexes: High Resolution Solid State 31P NMR Spectrum (Triphenylphosphine)Platinum(0)', J. Organo-metal. Chem., 280, 281-287 (1985).
- 94 H W Kroto, D McNaughton, L T Little and N Matthews, 'Long-Chain Hydrocarbon Molecules in the Interstellar Medium: Search for 1-cyanobut-3-ene-1-yne, CH2=CHC3N', Mon. Not. R. Astr. Soc., 213, 753-759 (1985).
- 95 M C Durrant, H W Kroto, D McNaughton and J F Nixon 'The New Molecule 1-Cyano-4-Phosphabutadiyne, NC4P, Produced by Copyrolysis of PC13L and CH3C3N: Detection and Vibration-Rotation Analysis by Microwave Spectroscopy', J. Mol. Spectrosc., 109, 8-14, (1985).
- 96 K Ohno, H Matsuura, D McNaughton and H W Kroto, 'Infrared Spectra of 1-Phosphapropyne, CH3CP, and its Perdeuteride CD3C=P', J. Mol. Spectrosc., 111, 415-424, (1985).
- 97 M A King, H W Kroto and B M Landsberg, 'Microwave Spectrum of the Quasilinear Molecule Cyanogen Isothiocyanate, NCNCS', J. Mol. Spectrosc., 113, 1-20, (1985).
- 98 H E Hosseini, H W Kroto, J F Nixon and O Ohashi, '13 31P, 19F and 1H NMR Spectroscopic study of the Reaction of Bis(Trifluoromethyl)Phosphine and solid KOH. Synthesis of the Phosphaalkene CF3P=CF2',J. Organometallic Chem., 296, 351-355, (1985).
- 99 H W Kroto and D McNaughton, 'Photoelectron Spectra of the Amino difluoroboranes NH2=BF2, NHMe=BF2: and NMe2=BF2', J. Chem. Soc. Dalton Trans., 1767. (1985)
- 100 H W Kroto, J R Heath, S C O'Brien, R F Curl and R E Smalley, 'C60: Buckminsterfullerene', Nature, 318(No.6042), 162-163,(1985) [cover illustration].
- 101 Lanthanum complexes of spheroidal carbon shells; J. R. Heath, S. C. O'Brien, Q. Zhang, Y. Liu, F. R. Curl, H. W. Kroto, F. K. Tittle and R. E. Smalley, *J. Am. Chem. Soc.*, **107**, 7779-7780 (1985).
- 102 Negative carbon cluster ion beams; new evidence for the special nature of  $C_{60}$ ; Y. Liu, S. C. O'Brien, Q. Zhang, J. R. Heath, F., K. Tittle, R. F. Curl, H. W. Kroto and R. E. Smalley, *Chem. Phys. Lett.*, **126**, 215-217 (1986).
- 103 Reactivity of large carbon clusters: spheroidal carbon shells and their possible relevance to the formation and morphology of soot; Q. L. Zhang, S. C. O'Brien, J. R. Heath, Y. Liu, R. F. Curl, H. W. Kroto and R. E. Smalley, *J. Phys. Chem.*, **90**, 525-528 (1986).

- 104 A reply to "Magic Numbers" in  $C_n^+$  and  $C_n^-$  abundance distributions based on experimental observations; S. C. O'Brien, J. R. Heath, H. W. Kroto, R. F. Curl and R. E. Smalley, *Chem. Phys. Lett.* **132**, 99-102 (1986).
- 105 Chemistry between the stars; H. W. Kroto, Proc. Roy. Institution, 58, 45-72 (1986)
- 106 The formation of long carbon chain molecules during laser vapourisation of graphite; J. R. Heath, Q. Zhang, S. C. O'Brien, R. F. Curl, H. W. Kroto and R. E. Smalley, *J. Am. Chem. Soc.*, **109**, 359-363, (1987).
- 107 The stability of the Fullerenes  $C_n$  (n = 24, 28, 32, 50, 60 and 70); H. W. Kroto, *Nature*, 329, 529-531 (1987).
- 108 Long carbon chain molecules in circumstellar shells; H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Astrophys. J.*, **314**, 352-355 (1987).
- 109 Carbon condensation; H. W. Kroto, Comments Cond. Mat. Phys., 13, 119-141 (1987).
- 110 Chains and grains in interstellar space; H. W. Kroto in A. Leger, L. d'Hendecourt and N. Boccara, *Polycyclic Aromatic Hydrocarbons and Astrophysics*, Reidel, 1987, pp197-206.
- 111 The formation of quasi-icosohedral spiral shell carbon particles; H.W. Kroto and K.G. McKay, *Nature*, **331**, 328-331 (1988).
- 112 Space, stars, C<sub>60</sub> and soot; H.W. Kroto, *Science*, **242**, 1139-1145 (1988).
- 113 C<sub>60</sub>: Buckminsterfullerene, other Fullerenes and the icospiral shell; H.W. Kroto, *Computers and Math. Applic.*, **17**, 417-423 (1988).
- 114 The chemistry of the interstellar medium; H.W. Kroto, *Phil. Trans. Roy. Soc.*, *Lond. A.*, 325, 405-421 (1988).
- 115 The role of linear and spheroidal carbon molecules in interstellar grain formation; H.W. Kroto, *Ann. Phys. Fr.*, **14**, 169-179 (1989).
- 116 Giant Fullerenes; H.W. Kroto, Chem. Brit., 26, 40-42 (1990)
- 117 Dust around AFGL 2688, molecular shielding, and the production of carbon chain molecules; M. Jura and H.W. Kroto, *Astrophys. J.*, **351**, 222-229 (1990).
- 118 C<sub>60</sub>, Fullerenes, giant Fullerenes and soot; H.W. Kroto, *Pure Appl. Chem.*, **62**, 407-415 (1990).
- 119 The formation and structure of interstellar dust; H.W. Kroto in S. Chang (Ed.) 'Carbon in the Galaxy'; Proc. Conf. NASA Aims Research Center, Nov 5-6 1987, Publ. 1990.
- 120 Possible assignment of the 11.3 m UIR feature in emission from soot-like microparticles with internal hydrogens, S.P. Balm and H.W. Kroto, *Mon. Not. Roy. Astronom. Soc.*, **245**, 193-197 (1990).
- 121 Isolation, separation and characterisation of the Fullerenes  $C_{60}$  and  $C_{70}$ ; the third form of carbon; R. Taylor, J.P. Hare, A.K. Abdul-Sada and H.W. Kroto, *J. Chem. Soc. Chem., Commun.*, 1423-14251 (1990).

- 122 Fullerene cage clusters. ☐ The key to the structure of solid carbon; H.W. Kroto, *J. Chem. Soc.*, *Faraday Trans.*, **86**, 2465-2468 (1990).
- 123 The discovery of carbon 60; H.W. Kroto, R. Taylor and D.R.M. Walton, *Univ. Sussex Ann. Rep.*, 6-8 (1990-91).
- 124 The analysis of comet mass spectrometric data; S.P. Balm, J.P. Hare and H.W. Kroto, Space Sci. Revs., **56**, 185-189 (1991)
- 125 Potential-energy function of large carbon clusters; S.P. Balm, A.W. Allaf, H.W. Kroto and J.N. Murrell, *J. Chem. Soc. Faraday Trans.*, **86**, 803-806 (1991).
- 126 Preparation and UV/VIS spectra of Fullerenes  $C_{60}$  and  $C_{70}$ ; J.P. Hare, H.W. Kroto and R. Taylor, *Chem. Phys. Lett.*, **177**, 394-398 (1991).
- 127 The IR spectra of Fullerene-60 and -70; J.P. Hare, T.J. Dennis, H.W. Kroto, R. Taylor, A.W. Allaf, S. Balm and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 412-413 (1991).
- 128 Thermodynamic evidence for a phase transition in crystalline fullerene C<sub>60</sub>; A. Dworkin, H. Szwarc, S. Leach, J.P. Hare, T.J. Dennis, H.W. Kroto, R. Taylor and D.R.M. Walton, *C. R. Acad., Sci. Paris, t.312, Ser II*, 979-982 (1991).
- 129 Degradation of C<sub>60</sub> by light; R. Taylor, J.P. Parsons, A.G. Avent, S.P. Rannard, T.J. Dennis, J.P. Hare, H.W. Kroto and D.R.M. Walton, *Nature*, **351**, 277 (1991).
- 130 Thermodynamic characterisation of the crystallinity of footballene  $C_{60}$ ; A. Dworkin, C. Fabre, D. Schutz, G. Kriza, R. Ceolin, H. Szwarc, P. Bernier, D. Jerome, S. Leach, A. Rassat, J.P. Hare, T.J. Dennis, H.W. Kroto, R. Taylor and D.R.M. Walton, *C. R. Acad., Sci. Paris, t.313, Ser II*, 1017 (1991).
- 131 Fluorination of Buckminsterfullerene; J.H. Holloway, E.G. Hope, R. Taylor, J.G. Langley, A.G. Avent, T.J. Dennis, J.P.Hare, H.W. Kroto and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 966-969 (1991).
- 132  $C_{60}$ : the celestial sphere that fell to earth; H.W. Kroto. Nanotechnology, 1, 1-2 (1991).
- 133 The magnetic circular dichroism and absorption spectra of  $C_{60}$  isolated in argon matrices; Z. Gasyna, P.N. Schatz, J.P. Hare, T.J. Dennis, H.W. Kroto, R. Taylor and D.R.M.Walton, *Chem. Phys. Lett.*, **183**, 283-291 (1991).
- 134 Hypothetical twisted structure for  $C_{60}F_{60}$ ; P.W. Fowler, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc. Faraday Trans.*, **87**, 2685-2686 (1991).
- 135 Crystal structure and bonding of ordered  $C_{60}$ ; W.I.F. David, R.M. Ibberson, J. Matthewman, K. Prassides, T.J. Dennis, J.P. Hare, H.W. Kroto, R. Taylor and D.R.M. Walton, *Nature*, **353**, 156-158 (1991).
- 136 Large infrared nonlinear optical response of C<sub>60</sub>; W.J. Blau, H.J. Byrne, D.J. Cardin, T.J. Dennis, J.P. Hare, J. Tomkinson, H.W. Kroto, R. Taylor and D.R.M. Walton, *Phys. Rev. Lett.*, **67**, 1423-1425 (1991).
- 137 The vibrational Raman spectra of  $C_{60}$  and  $C_{70}$ ; T.J. Dennis, J.P. Hare, H.W. Kroto, R.

- Taylor, D.R.M. Walton and P.J. Hendra, Spectrochim. Acta, 47A, 1289-1292 (1991).
- 138 Inelastic neutron scattering spectrum of the fullerene  $C_{60}$ ; K. Prassides, T.J.S. Dennis, J.P. Hare, J. Tomkinson, H.W. Kroto, R. Taylor and D.R.M. Walton, *Chem. Phys. Lett.*, **187**, 455-458 (1991).
- 139 C<sub>60</sub> Buckminsterfullerene; H W Kroto, A W Allaf and S P Balm, *Chem. Revs.*, **91**, 1213-1235 (1991)
- 140 Electronic spectra and transitions of the fullerene  $C_{60}$ ; S. Leach, M. Vervloet, A. Despres, E. Breheret, J.P. Hare, T.J. Dennis, H.W. Kroto, R. Taylor and D.R.M. Walton; *Chem. Phys.*, **160**, 451-466 (1992).
- 141 No lubricants from fluorinated C<sub>60</sub>; R. Taylor, A.G. Avent, T.J. Dennis, J.P. Hare, H.W. Kroto, D.R.M. Walton, J.H. Holloway, E.G. Hope, and G.J. Langley, *Nature*, **355**, 27 (1992).
- 142 C<sub>60</sub>: Buckminsterfullerene, the celestial sphere that fell to earth; H.W. Kroto, *Angew. Chem. Internat. Edit. Engl.*, **31**, 111-129 (1992).
- 143 A postbuckminsterfullerene view of carbon in the galaxy; J.P. Hare and H.W. Kroto, *Accounts Chem. Res.*, **25**, 106-112 (1992).
- 144 Nucleophilic substitution of fluorinated  $C_{60}$ ; R. Taylor, J.H. Holloway, E.G. Hope, A.J. Avent, G.J. Langley, T.J. Dennis, J.P. Hare, H.W. Kroto and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 665-667 (1992).
- 145 Formation of  $C_{60}Ph_{12}$  by electrophilic aromatic substitution; R. Taylor, G.J. Langley, M.F. Meidine, J.P. Parsons, A.K. Abdul-Sada, T.J. Dennis, J.P. Hare, H.W. Kroto and D.R.M.Walton, *J. Chem. Soc., Chem. Commun.*, 667-668 (1992).
- 146 The post-Buckminsterfullerene graphite horizon; H.W. Kroto, *J. Chem. Soc., Dalton Trans.*, 2141-2143 (1992)
- 147 Astrophysical Problems involving Carbon Re-appraised; J.P. Hare and H.W. Kroto in P.D. Singh (Ed.) 'Astrochemistry of cosmic phenomena' IAU, The Netherlands, 1992, pp. 47-54.
- 148 Fullerene physics; K. Prassides and H.W. Kroto, Physics World, 5, 44-49 (1992).
- 149 Preparation and characterisation of  $C_{60}Br_{6}$  and  $C_{60}Br_{8}$ ; P.R. Birkett, P.B. Hitchcock, H.W. Kroto, R. Taylor and D.R.M. Walton, *Nature*, **357**, 479-481 (1992).
- 150 Post-Fullerene organic chemistry; H.W. Kroto and D.R.M. Walton, in E. Osawa and O. Yonemitsu (Eds.), 'Carbocyclic cage compounds', VCH, 1992, pp 91-100.
- 151 A mass spectrometric/NMR study of Fullerene-78 isomers; R. Taylor, G.J. Langley, T.J.S. Dennis, H.W. Kroto and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 1043-1046 (1992).
- 152 Fullerenes: physics and astrophysics studies; H.W. Kroto, K. Prassides, M. Endo and M. Jura in C. Taliani, G. Ruani and R. Zamboni (Eds.) *Fullerenes; status and perspectives*, Proc. 1st Italian Workshop, Bologna (Feb. 6-7 1992) World Scientific Advanced Series in Fullerenes Vol.2, 1992, pp1-12.

- 153 Neutron scattering studies of Fullerenes and alkali-metal doped Fullerides, K. Prassides, C. Christides, J. Tomkinson, M.J. Rosseinsky, D.W. Murphy, R.C. Haddon, T.J.S. Dennis, J.P. Hare, H.W. Kroto, R. Taylor and D.R.M. Walton in C. Taliani, G. Ruani and R. Zamboni (Eds.) *Fullerenes; status and perspectives*, Proc. 1st Italian Workshop, Bologna (Feb. 6-7 1992) World Scientific Advanced Series in Fullerenes Vol. 2, 1992, pp147-160.
- 154 Single crystal x-ray structure of benzene-solvated  $C_{60}$ ; M.F. Meidine, P.B. Hitchcock, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 1534-1537 (1992).
- 155 Simulated transmission electron microscope images and characterisation of the 'lcospiral'; K.G. McKay, H.W. Kroto and D.J. Wales, *J. Chem. Soc. Faraday Trans.*, **88**, 2815-2821 (1992).
- 156 An end to the search for the ground state of C<sub>84</sub>?!... D.E. Manolopoulos, P.W. Fowler, R.Taylor, H.W. Kroto and D.R.M. Walton, *J. Chem. Soc. Faraday Trans.*, **88**, 3117-3118 (1992).
- 157 Isolation and spectroscopy of fullerenes; H.W. Kroto, K. Prassides, R. Taylor and D.R.M. Walton, *Physica Scripta*, **T45**, 314-318 (1992).
- 158 Circumstellar and interstellar fullerenes and their analogues; H.W. Kroto and M. Jura, Astron. Astrophys., 263, 275-280 (1992)
- 159 Introduction; H.W. Kroto, Carbon, 30, 1139-1141 (1992).
- 160 Fullerenes and fullerides in the solid state; neutron scattering studies; K. Prassides, H.W. Kroto, R. Taylor, D.R.M. Walton, W.I.F. David, J. Tomkinson, R C Haddon, M.J. Rosseinsky and D.W. Murphy, *Carbon*, **30**, 1277-1286 (1992).
- 161 Formation of carbon nanofibers; M Endo and H W Kroto, J. Phys. Chem., 96, 6941-6944 (1992).
- 162 Preparation and characterisation of C<sub>60</sub>(ferrocene)<sub>2</sub>; J.D. Crane, P.B. Hitchcock, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 1764-1765 (1992).
- 163 Mu@C<sub>70</sub>; monitoring the dynamics of fullerenes from inside the cage; K. Prassides, T.J.S. Dennis, C. Christidies, E. Roduner, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Phys. Chem.*, **96**, 10600-10602 (1992).
- 164 Isolation, characterisation and chemical reactions of fullerenes; R. Taylor, A.G. Avent, P.R. Birkett, T.J.S. Dennis, J.P. Hare, P.B. Hitchcock, J.H. Holloway, P.G. Hope, H.W. Kroto, G.J. Langley, M.F. Meidine, J.P. Parsons and D.R.M. Walton, *Pure Appl. Chem.*, **65**, 1351 (1992).
- 165 Discovery; H.W. Kroto, R. Taylor and D.R.M. Walton, *Univ. Sussex Ann. Rep.*, 6 (1992).
- 166 Hydrogenation of carbon clusters; A.W. Allaf, R.A. Hallett, S.P. Balm and H.W. Kroto, *Internat. J. Mod. Phys. B*, **6**, 3595 (1992).
- 167 Optical emission from carbon clusters in a supersonic expansion; S.P. Balm, R.A. Hallett, A.W. Allaf, A.J. Stace and H.W. Kroto, *Internat. J. Mod. Phys. B*, **6**, 3757 (1992).
- 168 Fullerene studies at Sussex; H.W. Kroto, K. Prassides, A.J. Stace, R. Taylor and

- D.R.M. Walton in W.E. Billups and M.A. Ciufolini (Eds.) *Buckminsterfullerenes*, VCH, 1993, Ch 2, pp 21-57.
- 169 The Raman spectra of  $C_{60}Br_{24}$ ,  $C_{60}Br_{8}$  and  $C_{60}Br_{6}$ ; P.R. Birkett, I. Gross, P.J. Hendra, H.W. Kroto, R. Taylor and D.R.M. Walton, *Chem. Phys. Lett.*, **205**, 399-404 (1993).
- 170 The structural characterisation of buckminsterfullerene compounds; P.R. Birkett, J.D. Crane, P.B. Hitchcock, H.W. Kroto, M.F. Meidine, R. Taylor and D.R.M. Walton, *J. Mol. Struct.*, **292**, 1 (1993)
- 171 Polyynes and the formation of fullerenes; H.W. Kroto and D.R.M. Walton, *Phil. Trans. Roy. Soc. Lond. Ser. A*, **343**, 103-112 (1993)
- 172 Highly oxygenated derivatives of fluorinated  $C_{60}$ , and the mode of fragmentation of the fluorinated cage under electron impact conditions; R. Taylor, G.J. Langley, A.K. Brisdon, J.H. Holloway, E.G. Hope, H.W. Kroto and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 875-878 (1993)
- 173  $^{13}$ C NMR spectroscopy of C<sub>76</sub>, C<sub>78</sub>, C<sub>84</sub>, and mixtures of C<sub>86</sub>-C<sub>102</sub>; anomalous chromatographic behaviour of C82 and evidence for C<sub>70</sub>H<sub>12</sub>; R. Taylor, G.J. Langley, A.G. Avent, T.J.S. Dennis, H.W. Kroto and D.R.M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1029 (1993).
- 174 Preparation and <sup>13</sup>C NMR characterisation of C<sub>60</sub>Cl<sub>6</sub>; P.R. Birkett, A.G. Avent, A.D. Darwish, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 1230 (1993).
- 175 Formation and stabilisation of the hexa-adduct of cyclopentadiene with  $C_{60}$ ; M.F. Meidine, R. Roers, G.J. Langley, A.G. Avent, A.D. Darwish, S. Firth, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 1342 (1993).
- 176 Preparation and single crystal structure determination of the solvated intercalate  $C_{60}$ - $I_2$ -toluene; P.R. Birkett, C. Christidies, P.B. Hitchcock, H.W. Kroto, K. Prassides, R. Taylor and D.R.M. Walton, *J. Chem. Soc.*, *Perkin 2*, 1407 (1993).
- 177 Enthalpies of formation of Buckminsterfullerene ( $C_{60}$ ) and of the parent ions  $C_{60}^+$ ,  $C_{60}^{-2+}$ ,  $C_{60}^{-3+}$  and  $C_{60}^-$ ; H.P. Diego, M.E.M. da Piedade, T.J.S. Dennis, J.P. Hare, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Faraday Trans.*, **89**, 3541, (1993).
- 178 The  $C_{60}$ -catalysed oxidation of hydrogen sulphide to sulphur; A.D. Darwish, H.W. Kroto, R. Taylor and D.R.M. Walton, *Fullerene Sci. & Tech.*, 1, 571 (1993).
- 179 Stable derivatives of small fullerenes; H.W. Kroto and D.R.M. Walton, *Chem. Phys. Lett.*, **214**, 353 (1993).
- 180 Isolation, characterisation and chemical reactions of fullerenes; R. Taylor, A.G. Avent, P.R. Birkett, T.J.S. Dennis, J.P. Hare, P.B. Hitchcock, J.H. Holloway, E.G. Hope, H.W. Kroto, G.J. Langley, M.F. Meidine, J.P. Parsons and D.R.M. Walton, *Pure Appl. Chem.*, **65**, 135 (1993).
- 181 Neutron scattering and SR studies of fullerenes and their derivatives; K. Prassides, *Physica Scripta*, **T49**, 735 (1993).

182 The production and structure of pyrolytic carbon nanotubes (PCNTs); M Endo, K Takeuchi, S Igarashi, K Kobori, M Shiraishi and H W Kroto, *J. Phys. Chem. Solids*, **54**, 1841 (1993)

Website Created And Maintained By: Christopher Dean This Page Last Updated 23/02/2003



Publications: 1994 - 2000

Years: 1963 - 1984 1985 - 1993 1994 - 2000 2001 - 2002

183 Formation of hydrides of fullerene- $C_{60}$  and  $C_{70}$ ; A.G. Avent, A.D. Darwish, D.K. Heimbach, H.W. Kroto, M.F. Meidine, J.P. Parsons, C. Remars, R. Roers, O. Ohashi, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Perkin Trans.* 2, 15 (1994).

184 Improved chromatographic separation of  $C_{60}$  and  $C_{70}$ ; A.D. Darwish, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 15 (1994).

185 The structure of C<sub>60</sub>Ph<sub>5</sub>Cl and C<sub>60</sub>Ph<sub>5</sub>H, formed via electrophilic aromatic substitution; A.G. Avent, P.R. Birkett, J.D. Crane, A.D. Darwish, G.J. Langley, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 1463 (1994).

186 Formation of fullerols via hydroboration of fullerene-C<sub>60</sub>; N.S. Schneider, A.D. Darwish, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 463 (1994).

187 Phosphorus/Buckminsterfullerene intercalation compound,  $C_{60}(P_4)_2$ ; I W Locke, A D Darwish, H W Kroto, K Prassides, R Taylor and D R M Walton; *Chem. Phys. Lett.*, **225**, 186 (1994)

188 Pentamethylcyclopentadiene adducts of [60]- and [70]fullerene; M F Meidine, A G Avent, A D Darwish, H W Kroto, O Ohashi, R Taylor and D R M Walton, *J. Chem. Soc. Dalton Trans. 2*, 1189 (1994)

189 Reaction of [70]Fullerene with benzyne; A.D. Darwish, A.K. Abdul-Sada, G.J. Langley, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, £2133 (1994).

190 The structure and reactivity of  $C_{60}$ ; H.W. Kroto, R. Taylor and D.R.M. Walton, *Pure Appl. Chem.*, **66**, 2091 (1994).

191 The fullerenes - precursors for 21st century materals; A.G Avent, P.R. Birkett, C. Christides, J.D. Crane, A.D. Darwish, P.B. Hitchcock, H.W. Kroto, K. Prassides, R. Taylor and D.R.M. Walton, *Pure Appl. Chem.*, **66**, 1389 (1994).

192 The structure of buckminsterfullerene compounds; A.G. Avent, P.R. Birkett, C. Christides, J.D. Crane, A.D. Darwish, P.B. Hitchcock, H.W. Kroto, M.F. Meidine, K. Prassides, R. Taylor and D.R.M. Walton, *J. Mol. Struct.*, **325**, 1 (1994).

193 *cis*-Bromine addition to the bicyclopentene addend on [60]Fullerene; M.F. Meidine, A.G. Avent, A.D. Darwish, G.J. Langley, W. Locke, O. Ohashi, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc. Perkin Trans 2*, 2125 (1994).

194 Smaller carbon species in the laboratory and space; H. W. Kroto, *Internat. J. Mass Spectrometry & Ion Processes*, **138**, 1 (1994).

- 195 The charisma of C<sub>60</sub> Buckminsterfullerene; H. W. Kroto, M.R.S. Bull., 19, 21 (1994).
- 196 New horizons in carbon chemistry and materials science; H.W. Kroto, J.P. Hare, A. Sarkar, K. Hsu, M. Terrones and J.R. Abeysinghe, *M.R.S. Bull.*, **19**, 51 (1994).
- 197 Formation of fullerene-C<sub>60</sub> by pyrolysis of naphthalene; R. Taylor, H.W. Kroto, D.R.M. Walton and G.J. Langley, *Mol. Mat.*, **4**, 7 (1994).
- 198 Phenylation of [60]fullerene; R. Taylor, A.G. Avent, P.R. Birkett, J.D. Crane, A.D. Darwish, G.J. Langley, H.W. Kroto and D.R.M. Walton; *Novel Forms of Carbon II, MRS.*, **349**, 107 (1994).
- 199 Oxygenated species in the products of fluorination of [60]- and [70] Fullerene by fluorine gas; R.Taylor, G.J. Langley, J.H. Holloway, E.G. Hope, A.K. Brisdon, H.W. Kroto and D.R.M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 181 (1995).
- 200 Formation of methylene adducts of [60]-, [70]-, [78]-, and [84]-fullerenes by reaction of fullerene-containing soot extract with THF; P.R. Birkett, A.D. Darwish, H.W. Kroto, G.J. Langley, R. Taylor and D.R.M. Walton, *J. Chem. Soc. Perkin Trans. 2*, 511 (1995).
- 201 Formation and characterisation of C<sub>70</sub>Cl<sub>10</sub>; P. R. Birkett, A.G. Avent, A.D. Darwish, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 683 (1995).
- 202 Theoretical characterisation of C<sub>70</sub>Cl<sub>10</sub>: the role of 1,4-addition across hexagonal rings; S.J. Austen, P.W. Fowler, J.P.B. Sandall, P.R. Birkett, A.G. Avent, A.D. Darwish, H.W.Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc. Perkin Trans 2*, 1027 (1995)
- 203 Hemi-toroidal networks in pyrolytic carbon nanotubes; A. Sarkar, M. Endo and H.W. Kroto, *Carbon*, **33** 51 (1995).
- 204 Holey fullerenes! A bis-lactone derivative of [70] fullerene with an 11-atom orifice; P.R. Birkett, A.G. Avent, A.D. Darwish, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 1869 (1995).
- 205 Condensed phase nanotubes; W.K. Hsu, J.P. Hare, M. Terrones, H.W. Kroto and D.R.M. Walton, *Nature*, **377**, 687 (1995).
- 206 Polyhydrogenation of [60]- and [70]- fullerenes; A.D. Darwish, A.K. Abdul-Sada, G.J. Langley, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc. Perkin Trans. 2*, 2359 (1995).
- 207 Reaction of [60]fullerene with triethylamine; J. Pola, A.D. Darwish, R.A. Jackson, H.W. Kroto, M.F. Meidine, A.J. Abdul-Sada, R. Taylor and D.R.M. Walton, *Fullerene Sci. Technol.*, **3**, 229 (1995)
- 208 Formation of [60]fullerene by pyrolysis of coranulene, 7,10-bis(2,2L-dibromovinyl)-fluoranthene and 11,12-benzofluoranthene; C.J. Crowley, H.W. Kroto, R. Taylor, D.R.M. Walton, M.S. Bratcher, P.-C. Cheng and L.T. Scott; *Tetrahedron Lett.*, 9215 (1995).
- 209 Physico-chemical studies on nanotubes and their encapsulated compounds; J.P. Hare, W.-K. Hsu, H.W.Kroto, A. Lappas, W.K. Maser, A.J. Pierik, K. Prassides, R. Taylor, M. Terrones and D.R.M. Walton in *Becent Advances in the Chemistry and Physics of Fullerenes and Related Materials* K.M. Kadisch and R.S. Ruoff (Eds), Electrochem. Soc., 2, 599-620 (1995).

- 210 Nanoscale encapsulation of molybdenum carbide in carbon clusters; J.P. Hare, W-K Hsu, H.W. Kroto, A. Lappas, K. Prassides, M. Terrones and D.R.M. Walton, *Chem. Mater.*, **8**, 6-8 (1996).
- 211 Synthesis and characterisation of the methanofullerenes,  $C_{60}(CHCN)$  and  $C_{60}(CBr_2)$ ; A.M. Benito, A.D. Darwish, H.W. Kroto, M.F. Meidine, R. Taylor and D.R.M. Walton, *Tetrahedron Lett.*, 1085-1086 (1996).
- 212 Formation of  $C_{70}Ph_{10}$  and  $C_{70}Ph_{8}$  from the electrophile  $C_{70}Cl_{10}$ ; P.R. Birkett, A.G. Avent, A.D. Darwish, H.W. Kroto, R. Taylor and D.R.M. Walton, *Tetrahedron*, **52**, 5235-5246 (1996).
- 213 Hydrogenation of [76]-, [78]- and [84]fullerenes; A.D. Darwish, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Perkin Trans. 2,* 1415-1418 (1996).
- 214 Polyhydrogenation of [60]- and [70]fullerenes with Zn/HCl and Zn/DCl; A.D. Darwish, H.W. Kroto, R. Taylor and D.R.M. Walton, *Synthetic Mets.*, 77, 303-307 (1996).
- 215 Recent developments in hydrogenation and arylation of [60]- and [70] fullerenes, A.G. Avent, P.R. Birkett, A.D. Darwish, H.W. Kroto, R. Taylor and D.R.M. Walton, *Mol. Mat.*, 7, 33-40 (1996).
- 216 Preparation and characterisation of C<sub>70</sub>Ph<sub>9</sub>OH: the first fullerene with a single hydroxy group attached to the cage; P.R. Birkett, A.G. Avent, A.D. Darwish, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc. Chem. Commun.*, 1231-1232 (1996).
- 217 Electrical, magnetic and structural characterisation of fullerene soots; L.J. Dunne, A.K. Sarkar, H.W. Kroto, J. Munn, P. Kathirgamanathan, U. Heinen, J. Fernandez, J.P. Hare, D.G. Reid and A.D. Clark, *J. Physics-Condensed Matter*, **8**, 2127-2141 (1996).
- 218 Fullerene-based materials science at Sussex, J.P. Hare, W-K. Hsu, M. Terrones, A. Sarkar, S.G. Firth, A. Lappas, R. Abeysinghe, H.W. Kroto, K. Prassides, R. Taylor and D.R.M. Walton, *Mol. Mat.*, 7, 17-22 (1996).
- 219 Regiochemical clustering in halogenation of  $C_{60}$  and  $C_{70}$ ; P.R. Birkett, H.W. Kroto, R.Taylor and D.R.M. Walton, *Mol. Mat.*, **7**, 27-32 (1996).
- 220 Pyrolytic production of fullerenes; C.J. Crowley, R. Taylor, H.W. Kroto, D.R.M. Walton, P-C. Cheng and L.T. Scott, *Synth. Mets.*, **77**, 17-22 (1996).
- 221 Chlorination and arylation of [60]- and [70]fullerenes; P.R. Birkett, A.D. Darwish, A.G. Avent, H.W. Kroto, R. Taylor and D.R.M. Walton, *Proc. NATO Workshop*, **316**, 199-213 (1996).
- 222 Graphitic structures: from planar to spheres, toroids and helices; M Terrones, W-K Hsu, J P Hare, H W Kroto, H Terrones and D R M Walton, *Phil. Trans. Roy. Soc. Lond.*, **A354**, 2025-2054 (1996).
- 223 Pyrolytically grown B<sub>x</sub>C<sub>y</sub>N<sub>z</sub> nanomaterials: nanofibres and nanotubes; M Terrones, A M Benito, C Manteca-Diego, W-K Hsu, O I Osman, J P Hare, D G Reid, H Terrones, A K Cheetham, H W Kroto and D R M Walton, *Chem. Phys. Lett.*, **257**, 576-582 (1996).
- 224 Metal particle catalysed production of nanoscale BN structures; M Terrones, W-K Hsu, H Terrones, J P Zhang, S Ramos, J P Hare, R Castillo, K Prassides, A K Cheetham, H W

- Kroto and D R M Walton, Chem. Phys. Lett., 259, 568-573 (1996).
- 225 Production of carbon nanotubes and graphitic onions by condensed phase electrolysis; W-K Hsu, J P Hare, D G Reid, H W Kroto and D R M Walton in H Kuzmany, J Fink, M Mehring and S Roth (Eds), *Fullerenes and Fullerene Structures*, World Scientific, 1996, pp 226-231.
- 226 Morphology effects of catalytic particles in pyrolytic grown  $B_x C_y N_z \Box$  nanofibres and nanotubes; M Terrones, A N Benito, W K Hsu, O I Osman, J P Hare, D G Reid, K Prassides, H W Kroto, C Manteca-Diego, H Terrones and D R M Walton in H Kusmany, J Fink, M Mehring and S Roth (Eds), *Fullerenes and Fullerene Structures*, World Scientific, 1996, pp 243-249.
- 227 Electrolytic formation of carbon nanostructures; W-K Hsu, M Terrones, J P Hare, H Terrones, H W Kroto and D R M Walton, *Chem. Phys. Lett.*, **262**, 161-166 (1996).
- 228 Phosphine-catalysed cycloaddition of buta-2,3-dienoates and but-2-ynoates with [60] fullerene; B F OLDonovan, P B Hitchcock, M F Meidine, H W Kroto, R Taylor and D R M Walton, J. Chem. Soc., Chem. Commun., 81-82 (1997).
- 229 Platinum(0)-[60]fullerene complexes with chelating phosphine ligands.  $\square$  Synthesis and characterisation of  $(\eta-C_{60})$ Pt(P-P) [P-P = dppe, dppp]; M van Wijnkoop, M F Meidine, A G Avent, A D Darwish, H W Kroto, R Taylor and D R M Walton, *J. Chem. Soc. Dalton Trans.*, 675-676 (1997).
- 230 Preparation and characterisation of unsymmetrical  $C_{60}$ Ph<sub>4</sub> and symmetrical  $C_{60}$ Ph<sub>2</sub>: the effect of regoselective attack upon  $C_{60}$ Cl<sub>6</sub>; P R Birkett, A G Avent, A D Darwish, H W Kroto, R Taylor, D R M Walton, *J. Chem. Soc. Perkin Trans. 2*, 457-461 (1997)
- 231 Arylation of [60] fullerene via electrophilic aromatic substitution involving the electrophile  $C_{60}Cl_6$ : frontside nucleophilic substitution of fullerenes; PR Birkett, AG Avent, AD Darwish, I Hahn, HW Kroto, GJ Langley, JOL Loughlin, R Taylor and DR M Walton, *J. Chem. Soc. Perkin Trans. 2*, 1121 (1997)
- 232 Synthesis of nanotubes *via* catalytic pyrolysis of acetylene: a SEM study; T E Miller, D G Reid, W K Hsu, J P Hare, H W Kroto and D R M Walton, *Carbon*, **35**, 951 (1997)
- 233 Controlled production of aligned-nanotube bundles; M Terrones, N Grobert, J Olivares, J P Zhang, H Terrones, K Kordatos, W K Hsu, J P Hare, P D Townsend, K Prassides, A Cheetham, H W Kroto and D R M Walton, *Nature*, 388, 52 (1997)
- 234 The Diels-Alder adduct of C<sub>70</sub>Ph<sub>8</sub> with anthracene; A G Avent, P R Birkett, A D Darwish, H W Kroto, R Taylor and D R M Walton, *Fullerene Sci. Technol.*, **5**, 643 (1997)
- 235 Arylation of  $\mathrm{Br_2/FeCl_3/PhH}$ : formation of  $\mathrm{C_{58}}$  derivatives *via* CO loss; A D Darwish, P R Birkett, G J Langley, H W Kroto, R Taylor and D R M Walton, *Fullerene Sci. Technol.*, **5**, 705 (1997)
- 236 Synthetic routes to novel nanomaterials; with M Terrones, W K Hsu, J P Hare, H W Kroto and D R M Walton, Fullerene Sci. Technol., 5 813 (1997)
- 237 The structure of fullerene compounds; with A G Avent, A M Benito, P R Birkett, A D Darwish, P B Hitchcock, H W Kroto, I W Locke, M F Meidine, B F O Donovan, K Prassides, R Taylor, M van Wijnkoop and D R M Walton, J. Mol. Struct., 436-437, 1-9 (1997)

- 238 Transition metal surface decorated fullerene as possible catalytic agents for the creation of single-walled nanotubes of uniformed diameter; P R Birkett, A J Cheetham, B R Eggen, J P Hare, H W Kroto and D R M Walton, *Chem. Phys. Lett.*, **281**, 111-114 (1997)
- 239 Symmetry, space, stars and C<sub>60</sub>; H W Kroto, *Angew. Chem. Int. Ed. Engl.*, **36**, 1578 (1997), also *Rev. Modern Physics*, **69**, 703 (1997). ☐ Nobel lectures in Chemistry 1996. Solid azafullerenes and azafullerides; K Prassides, F Wudl and W Andreoni, *Fullerene Sci. Technol.*, **5**, 801-812 (1997)
- 240 Fullerenes; K Prassides, Current Opinion in Solid State and Materials Science, 2, 433-439 (1997)
- 241 Spontaneous oxidation of  $C_{60}Ph_5X$  (X = H, Cl) to a benzo[*b*]furanyl[60]fullerene; A G Avent, P R Birkett, A D Darwish, H W Kroto, R Taylor and D R M Walton, *J. Chem. Soc., Chem. Comm* $\subseteq un.$ , 1579-1580 (1997)
- 242 Novel nanotubes and encapsulated nanowires; M Terrones, W K Hsu, A Schilder, H Terrones, N Grobert, J P Hare, Y Q Zhu, M Schwoerer, K Prassides, H W Kroto and D R M Walton, *Appl. Phys. A*, **66**, 307-317 (1998)
- 243 Novel formation of a phenylated isoquinolino[3:,4::1,2][60]fullerene; A K Abdul-Sada, A G Avent, P R Birkett, A D Darwish, H W Kroto, R Taylor, D R M Walton and O B Woodhouse, J. Chem. Soc., Chem. Commun., 307-308 (1998)
- 244 A hexaallyl[60]fullerene, C<sub>60</sub>(CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>6</sub>; A K Abdul-Sada, A G Avent, P R Birkett, H W Kroto, R Taylor and D R M Walton, *J. Chem. Soc., Perkin Trans.* 1, 393-395 (1998).
- 245 Electrochemical formation of novel nanowires and their dynamic effects; W K Hsu, M Terrones, H Terrones, N Grobert, A I Kirkland, J P Hare, K Prassides, P D Townsend, H W Kroto and D R M Walton, *Chem. Phys. Lett.*, **284**, 177-183 (1998).
- 246 Preparation of aligned carbon nanotubes catalysed by laser-etched cobalt thin films; M Terrones, N Grobert, J P Zhang, H Terrones, J Olivares, W K Hsu, J P Hare, A K Cheetham, H W Kroto and D R M Walton, *Chem. Phys. Lett.*, **285**, 299-305 (1998)
- 247 3D silicon oxide nanostructures from nanoflowers to radiolaria; Y Q Zhu, W K Hsu, M Terrones, N Grobert, H Terrones, J P Hare, H W Kroto and D R M Walton, *J. Mater. Chem.*, **8**, 1859-1862 (1998)
- 248 Pyrolysis of  $C_{60}$ -thin films yields Ni-filled sharp nanotubes; N Grobert, M Terrones, A J Osborne, H Terrones, W K Hsu, S Trasobares, Y Q Zhu, J P Hare, H W Kroto and D R M Walton, in H Kuzmany *et al.* (Eds) *Proc. XII Internat. Winterschool on Electronic Properties of Novel Materials Progress in Molecular Nanostructures*, AIP Conf. Proc. 442, 1998, p 25
- 249 Nanotechnology of nanotubes and nanowires: from aligned carbon nanotubes to silicon oxide nanowires; N Grobert, J P Hare, W K Hsu, H W Kroto, A J Pidduck, C L Reeves, H Terrones, M Terrones, S Trasobares, C Vizard, D J Wallis, D R M Walton, P J Wright and Y Q Zhu, in H Kuzmany et al. (Eds) Proc. XII Internat. Winterschool on Electronic Properties of Novel Materials Progress in Molecular Nanostructures, AIP Conf. Proc. 442, 1998, p 29
- 250 Stable [60]fullerene carbocations; A G Avent, P R Birkett, H W Kroto, R Taylor and D R M Walton, *Chem. Commun.*, 2153-2154 (1998)
- 251 Functionalised fullerenes on silicon surfaces; M D Upward, P Moriarty, P H Beton, P R Birkett, H W Kroto, R Taylor and D R M Walton, *Surface Sci.*, **405**, 526-531 (1998)

- 252 Photophysical properties of some hexa-functionalized C<sub>60</sub> derivatives; P.-F Coheur, J Cornil, D A dos Santos, P R Birkett, J Li Li vin, J L Br das, J.-M. Janot, P Seta, S Leach, D R M Walton, R Taylor, H W Kroto and R Colin, *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, Electrochem. Soc., 6, 1140 (1998)
- 253 Thermolysis of  $C_{60}$  thin films yields Ni-filled tapered nanotubes; N Grobert, M Terrones, A J Osborne, H Terrones, W K Hsu, S Trasobares, Y Q Zhu, J P Hare, H W Kroto, D R M Walton, *Appl. Phys. A*, **67**, 595 (1998)
- 254 Nanotubes: A revolution in materials science and electronics; M Terrones, W K Hsu, H W Kroto and D R M Walton, in A Hirsch (Ed) *Topics in Current Chemistry*, **199**, 189-234 (1998)
- 255 Electrochemical production of low-melting metal nanowires; W K Hsu, J Li, H Terrones, M Terrones, N Grobert, Y Q Zhu, S Trasobares, J P Hare, C J Pickett, H W Kroto and D R M Walton, *Chem. Phys. Lett.*, **301**, 159-166 (1999)
- 256 Large-scale synthesis of carbon nanotubes by pyrolysis; K Tanaka, M Endo, K Takeuchi, W K Hsu, H W Kroto, M Terrones and D R M Walton, *The Science and Technology of Carbon Nanotubes*, K Tanaka, T Yamabe and K Fukui (Eds) Elsevier, 1999, Ch 11, pp 143-152
- 257 Solid phase production of carbon nanotubes; W K Hsu, Y Q Zhu, S Trasobares, H Terrones, M Terrones, N Grobert, H Takikawa, J P Hare, H W Kroto and D R M Walton, Appl. Phys. A, Rapid Commun., 68, 493 (1999)
- 258 New science for new materials; J P Attfield, R L Johnston, H W Kroto and K Prassides, in N Hall (Ed.), *The Age of the Molecule*, Royal Society of Chemistry, London, 1999, pp 181-208.
- 259 Carbon nitride nanocomposites: formation of aligned C<sub>x</sub>N<sub>y</sub> nanofibres; M Terrones, P Redlich, N Grobert, S Trasobares, W K Hsu, H Terrones, Y Q Zhu, J P Hare, C L Reeves, A K Cheetham, M Righle, H W Kroto and D R M Walton, *Advan. Mater.*, **11**, 655-658 (1999)
- 260 Photophysical properties of  $C_{60}Cl_6$ ,  $C_{60}Ph_5Cl$  and  $C_{60}Ph_5H$ ; P-F Coheur, J Cornil, D A dos Santos, P R Birkett, J LiL vin, J L Br L das, J-M Janot, P Seta, S Leach, D R M Walton, R Taylor, H W Kroto and R Colin, *Synthetic Mets*, **103**, 2407-2410 (1999)
- 261 Advances in the creation of filled nanotubes and novel nanowires; M Terrones, N Grobert, W K Hsu, Y Q Zhu, W B Hu, H Terrones, J P Hare, H W Kroto and D R M Walton, MRS Bull., 24, 43-49 (1999)
- 262 Tungsten oxide tree-like structures; Y Q Zhu, W Hu, W K Hsu, M Terrones, N Grobert, J P Hare, H W Kroto, D R M Walton and H Terrones, *Chem. Phys. Lett.*, **309**, 327-334 (1999)
- 263 Electrolytic formation of carbon-sheathed mixed Sn-Pb-nanowires; W K Hsu, S Trasobares, H Terrones, M Terrones, N Grobert, Y Q Zhu, W Z Li, R Escudero, J P Hare, H W Kroto and D R M Walton, *Chem. Mater.*, **11**, 1747-1751 (1999)
- 264 A simple route to silicon-based nanostructures; Y Q Zhu, W B Hu, W K Hsu, M Terrones, N Grobert, T Karali, H Terrones, J P Hare, P D Townsend, H W Kroto and D R M Walton, *Advan. Mater.*, **11**, 844-847 (1999)
- 265 Microscopy study of the growth process and structural features of silicon oxide nanoflowers; Y Q Zhu, W K Hsu, M Terrones, N Grobert, W B Hu, J P Hare, H W Kroto and

- D R M Walton, Chem. Mater., 11, 2709-2715 (1999)
- 266 Stable BC<sub>2</sub>N nanostructures; low temperature production of segregated C/BN layered materials; Ph. Kohler-Redlich, M Terrones, C Manteca-Deigo, W K Hsu, H Terrones, M Righle, H W Kroto and D R M Walton, *Chem. Phys. Lett.*, **310**, 459-465 (1999)
- 267 Enhanced magnetic coercivities in Fe nanowires; N Grobert, M Terrones, Ph Redlich, H Terrones, R Escudero, F Morales, W K Hsu, Y Q Zhu, J P Hare, M RL hle, H W Kroto and D R M Walton, *Appl. Phys. Lett.*, **75**, 3363-3364 (1999)
- 268 SiC-SiO<sub>x</sub> heterojunctions in nanowires; Y Q Zhu, W B Hu, W K Hsu, M Terrones, N Grobert, J P Hare, H W Kroto and D R M Walton, *J. Mater. Chem.*, **9**, 3173-3178 (1999)
- 269 An efficient route to large arrays of CN<sub>x</sub> nanofibres by pyrolysis of ferrocene/melamine mixtures; MTerrones, H Terrones, N Grobert, W K Hsu, Y Q Zhu, J P Hare, H W Kroto, D R M Walton, Ph Kohler-Redlich, M RI hle, J P Zhang and A K Cheetham, *Appl. Phys. Lett.*, **75**, 3932-3934 (1999)
- 270 Novel base-catalysed formation of benzo(b)furano[60]- and [70] fullerenes; A D Darwish, A G Avent, H W Kroto, R Taylor and D R M Walton, *J. Chem. Soc., Perkin Trans.* 2, 1983-1988 (1999)
- 271 New advances in the creation of nanostructured materials; N Grobert, J P Hare, W-K Hsu, H W Kroto, M Terrones, D R M Walton and Y K Zhu, *Pure Appl. Chem.*, **71**, 2125-2130 (1999)
- 272 A novel route to aligned nanotubes and nanofibres using láser patterned catalytic substrates; N Grobert, M Terrones, S Trasobares, K Kordatos, H Terrones, J Olivares, J P Zhang, Ph Redlich, W K Hsu, C L Reeves, D J Wallis, Y Q Zhu, J P Hare, A J Pidduck, H W Kroto and D R M Walton, *Appl. Phys. A.*, **70**, 175-183 (2000)
- 273 Generation of hollow crystalline tungsten oxide fibres; W B Hu, Y Q Zhu, W K Hsu, B H Chang, M Terrones, N Grobert, H Terrones, J P Hare, H W Kroto and D R M Walton, *Appl. Phys. A*, **70**, 231-
- 274 NaCl crystallisation within the space between carbon nanotube walls; W K Hsu, W Z Li, Y Q Zhu, M Terrones, H Terrones, N Yao, J P Zhang, S Firth, R J H Clark, N Grobert, □ A K Cheetham, H W Kroto and D R M Walton, *Chem. Phys. Lett.*, **317**, 77-82 (2000)
- 275 Boron-doping effects in carbon nanotubes; W K Hsu, S Firth, Ph Redlich, M Terrones, H Terrones, Y Q Zhu, N Grobert, A Schilder, R J H Clark, H W Kroto and D R M Walton, D. Mater. Chem., 10, 1425-1429 (2000)
- 276 Self-assembly of Si nanostructures; Y Q Zhu, W K Hsu, N Grobert, M Terrones, H Terrones, H W Kroto, D R M Walton and B Q Wei, *Chem. Phys. Lett.*, **322**, 312-320 (2000)
- 277 J L Brt. das, D R M Walton, R Taylor, H W Kroto and R Colin, J. Chem. Phys., 112, 6371-6781 (2000)
- 278 Production of WS<sub>2</sub> nanotubes; Y Q Zhu, W K Hsu, N Grobert, B H Chang, M Terrones, H Terrones, H W Kroto, D R M Walton and B Q Wei, *Chem. Mater.*, **12**, 1190 (2000)
- 279 Carbon nanotubes as nanoreactors for boriding iron nanowires; W-Q Han, P K Redlich, C Scheu, F Ernst, M Richle, N Grobert, M Terrones, H W Kroto and D R M Walton, *Adv. Mater.*, **12**, 1356-1359 (2000)

- 280 Metallic behaviour of boron-containing carbon nanotubes; W K Hsu, S Y Chu, E Munoz-Picone, J L Boldu, S Firth, P Franchi, P B Roberts, A Schilder, H Terrones, N Grobert, Y Q Zhu, M Terrones, M E McHenry, H W Kroto and D R M Walton, *Chem. Phys. Lett.*, 323, 572-579 (2000)
- 281 An alternative route to molybdenum disulfide nanotubes; W K Hsu, B H Chang, Y Q Zhu, L Y Q Han, H Terrones, M Terrones, N Grobert, A K Cheetham, H W Kroto and D R M Walton, J. Am. Chem. Soc., 122, 10155-10158 (2000)
- 282 Morphology, structure and growth of WS<sub>2</sub> nanotubes; Y Q Zhu, W K Hsu, H Terrones, N Grobert, B H Chang, M Terrones, B Q Wei, H W Kroto, D R M Walton, C B Boothroyd, I Kinlock, G Z Chen, A H Windle and D J Fray, *J. Mater. Chem.* 10, 2570-2577 (2000)
- 283 Mixed phase W<sub>x</sub>Mo<sub>y</sub>C<sub>z</sub>S<sub>2</sub> nanotubes; W K Hsu, Y Q Zhu, C B Boothroyd, I Kinloch, S Trasobares, H Terrones, N Grobert, M Terrones, R Escudero, G Z Chen, C Colliex, □ A H Windle, D J Fray, H W Kroto and D R M Walton, *Chem. Mater.*, **12**, 3541-3546 (2000)
- 284 C-MoS<sub>2</sub> and C-WS<sub>2</sub> nanocomposites; W K Hsu, Y Q Zhu, H W Kroto, D R M Walton, B Kamalakaran, M Terrones, *Appl. Phys. Lett.*, **77**, 4130-4132 (2000)
- 285 Aligned  $CN_x$  nanotubes by pyrolysis of ferrocene/ $C_{60}$  under  $NH_3$  atmosphere; W-Q Han, P Kohler-Redlich, T Seeger, F Ernst, M Rühle, N Grobert, W-K Hsu, B-H Chang, Y-Q Zhu, H W Kroto, D R M Walton, M Terrones and H Terrones, *Appl. Phys. Lett.*, 77, 1807-1809 (2000)
- 286 C<sub>60</sub>F<sub>18</sub>O, the first characterised intramolecular fullerene ether; O V Boltalina, B de La Vaissi⊡, P W Fowler, P B Hitchcock, J P B Sandell, P A Troshin and R Taylor, *Chem. Commun.*, 1325 (2000)
- 287 Cathodoluminescence of fullerene C<sub>60</sub>; A P Rowlands, T Karali, M Terrones, N Grobert, P D Townsend and K Kordatos, *J. Phys. Condensed Matter*, **12**, 7869-7878 (2000)
- 288 Photophysical properties of hexa-functionalised  $C_{60}$  derivatives: spectroscopic and quantum-chemical investigations; P-F Coheur, J Cornil, D A dos Santos, P R Birkett, J Li $\sqsubseteq$ vin, J L Br $\_$ das, D R M Walton, R Taylor, H W Kroto and R Colin, *J. Chem. Phys.*, **112**, 8555 (2000)

Website Created And Maintained By: Christopher Dean This Page Last Updated 23/02/2003



**Publications: 2001 - 2002** 

Years: 1963 - 1984 1985 - 1993 1994 - 2000 2001 - 2002

289 W<sub>x</sub>Mo<sub>y</sub>C<sub>z</sub>S<sub>2</sub> nanotubes; W K Hsu, Y Q Zhu, S Firth, M Terrones, H Terrones, S Trasobares, R J H Clark, H W Kroto and D R M Walton; *Carbon*, **39**, 1103-1116 (2001)

290 Tungsten-niobium-sulfur composite nanotubes; Y Q Zhu, W K Hsu, M Terrones, S Firth, N Grobert, R J H Clark, H W Kroto and D R M Walton, *Chem. Comm.*, 121-122 (2001)

291 Preparation and characterisation of two [70]fullerene diols, C<sub>70</sub>Ph<sub>8</sub>(OH)<sub>2</sub>; A G Avent, P R Birkett, A D Darwish, H W Kroto, R Taylor and D R M Walton, *J. Chem. Soc., Perkin Trans. 2,* 68 (2001)

292 Titanium-doped molybdenum disulfide nanostructures; W K Hsu, Y Q Zhu, N Yao, S Firth, L. E R J H Clark, H W Kroto and D R M Walton, Adv. Functional Mat., 11, 69 (2001)

293 Pyrolytic production of aligned carbon nanotubes from homogeneously dispersed benzene-based aerosols; M Mayne, N Grobert, M Terrones, R Kamalakaran, M R⊡hle, H W Kroto and D R M Walton, *Chem. Phys. Lett.*, **338**, 101-107 (2001)

294 Nb-doped WS<sub>2</sub> nanotubes; Y Q Zhu, W K Hsu, S Firth, M Terrones, R J H Clark, H W Kroto and D R M Walton, *Chem. Phys. Lett.*, **342**, 15-21 (2001)

295 A low resistence boron-doped carbon nanotube-polystyrene complex; P C P Watts, W K Hsu, G Z Cheng, D J Fray, H W Kroto and D R M Walton, *J. Mat. Chem.*, **11**, 2482 (2001)

296 Electron beam puncturing of carbon nanotube containers for release of stored nitrogen gas; Lieur S Trasobares, O Stephan, C Colliex, G Hug, W K Hsu, H W Kroto and D R M Walton, Eur. Phys. J B, 22, 117 (2001)

297 Tungsten disulphide sheathed carbon nanotubes; R L D Whitby, W K Hsu, P K Fearon, H W Kroto, D R M Walton and C B Boothroyd, *Chem. Phys. Chem.*, **2**, 620 (2001)

298 SiO<sub>x</sub>-coating of carbon nanotubes at room temperature; T Seeger, Ph Redlich, N Grobert, M Terrones, D R M Walton, H W Kroto and M R⊡hle, *Chem. Phys. Lett.*, **339**, 41-46 (2001)

299 Carbon nanotube templated promoted growth of NbS<sub>2</sub> nanotubes/nanorods; Y Q Zhu, W K Hsu, H W Kroto and D R M Walton, *Chem. Comm.*, 2184 (2001)

300 Selective Co-catalysed growth of novel MgO fishbone fractal nanostructures; Y Q Zhu, W K Hsu, W Z Zhou, M Terrones, H W Kroto and D R M Walton, *Chem. Phys. Lett.*, **347**, 337 (2001)

- 301 Novel nanostructures: from metal-filled carbon nanotubes to MgO nanoferns; N Grobert, EEEE W K Hsu, H W Kroto, M Mayne, M Terrones, P C P Watts, R L D Whitby, D R M Walton and Y Q Zhu, in *Perspectives of Fullerene Nanotechnology*, E Osawa (Ed), *Kluwer AP* (proofs 09 Oct 2001)
- 302 Some 4-fluorophenyl derivatives of [60] fullerene: oxide-induced fragmentation to  $C_{58}$ ; A D Darwish, A G Avent, P R Birkett, H W Kroto, R Taylor and D R M Walton, *J. Chem. Soc., Perkin Trans. 2,* 782 (2001)
- 303 WS<sub>2</sub> nanotubes containing single-walled carbon nanotube bundles; R L D Whitby, W K Hsu, P C P Watts, H W Kroto and D R M Walton, *Appl. Phys. Lett.*, **79**, 4574 (2001)
- 304 Complex WS<sub>2</sub> nanostructures; R L D Whitby, W K Hsu, T H Lee, C B Boothroyd, H W Kroto and D R M Walton, *Chem. Phys. Lett., (proofs 13 May 2002)*
- 305 Camphor-based carbon nanotubes as an anode in lithium secondary batteries; M Sharon, W K Hsu, H W Kroto, D R M Walton, A Kawahara, T Ishihara and Y Takita, J. Power Sources, 104, 148 (2002)
- 306 Field emission from non-aligned carbon nanotubes embedded in a polystyrene matrix; C H Poa, S R P Silva, P C P Watts, W K Hsu, H W Kroto and D R M Walton, *Appl. Phys. Lett., (proofs checked 04 April 2002)*
- 307 Novel SiO<sub>x</sub>-coated carbon nanotubes; M R⊡hle, T Seeger, Ph Redlich, N Grobert, □ M Terrones, D R M Walton and H W Kroto, *J. Ceramic Processing Research*, **3**, 1 (2002)
- 308 Multi-walled carbon nanotubes coated with tungsten disulphide; R L D Whitby, W K Hsu, P K Fearon, N C Billingham, I Maurin, H W Kroto, D R M Walton, C B Boothroyd, S Firth, R J H Clark and D Collison, *Chem. Mater.*, **14**, 2209 (2002)
- 309 Compartmentalised  $\rm CN_x$  nanotubes; Chemistry, morphology and growth; S Trasobares, O Stephan, G Hug, C Colliex, W K Hsu, H W Kroto and D R M Walton, *J. Chem. Phys.*, **116**, 8966 (2002)
- 310 Hollow cathode plasma synthesis of carbon nanofiber arrays at low temperature; A Huczko, H Lange, M Sioda, Y Q Zhu, W K Hsu, H W Kroto and D R M Walton, *J. Chem. Phys.*, **106**, 1534 (2002)
- 311 Tungsten disulphide coated multi-walled carbon nanotubes; R L D Whitby, W K Hsu, C B Boothroyd, H W Kroto and D R M Walton, Chem. Phys. Lett., (proofs 16 May)
- 312 WS<sub>2</sub> layer formation on multi-walled carbon nanotubes; R L D Whitby, W K Hsu, C B Boothroyd, K S Brigatti, H W Kroto and D R M Walton, *Appl. Phys. A*, (submitted 11 June 2002)
- 313 Novel ceramic nanostructures generated by arc-discharge; Y Q Zhu, H W Kroto, □ D R M Walton, H Langer and A Huczko, Chem. Phys. Lett., (submitted 10 June 2002)
- 314 Carbon nanotube composites as electrodes for salt water batteries; P C P Watts, U S F A Acquah, W K Hsu, J P Hare, H W Kroto and D R M Walton, J. Mater. Chem., (submitted 18 June 2002)
- 315 An alternative route to  $NbS_2$  nanotubes; Y Q Zhu, W K Hsu, H W Kroto and D R M Walton, J. Phys. Chem. B., (accepted 10 June 2002)

316 Conversion of amorphous  $WO_{3-x}$  into  $WS_2$  nanotubes; R L D Whitby, W K Hsu, H W Kroto and D R M Walton, *Phys. Chem. Chem. Phys.*, (submitted 18 June 2002)

Website Created And Maintained By: Christopher Dean This Page Last Updated 23/02/2003

# C<sub>60</sub>: Buckminsterfullerene

Chem. Rev. 1991, 91, 1213-1235

H. W. KROTO. A. W. ALLAF, and S. P. BALM

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

Received May 2, 1991 (Revised Manuscript Received July 26, 1921

#### Contents

	1213
Introduction     Summary of Relevant Carbon Studies Prior to	1214
the Discovery of C <sub>80</sub> Stability  III. The Discovery of C <sub>80</sub> : Buckminsterfullerene	1215
III. The Discovery of Sec.	1217
IV. Sources of Coo	1218
V. Stability and Intrinsic Properties of Ceo	1221
VI. Reaction Studies VII. Gas-Phase Carbon Nucleation and C <sub>60</sub>	1221
Exemption .	1223
VIII. Theoretical Studies of the Fullerenes IX. Isolation, Separation, and Structural	1226
IX. Isolation, Separation of Fullerene-60 and -70  X. Postbuckminsterfullerene Research—The First	1227
Docuits	1230
XI. Astrophysical Implications of C <sub>60</sub>	123
VII Conclusions	•

### 1. Introduction

a a garage property of the contraction

In 1967 Palmer and Shelef wrote the definitive review of the early work on carbon clusters in their article on the composition of carbon vapor. Major advances have however been made in the interim period, and the overall situation has been updated by Weltner and Van Zee2 who have given a very complete picture of the state of this fascinating field. Although Weltner and Van Zee's review is comprehensive (up to Nov 1, 1988). covering all aspects of carbon cluster properties, recent advances in the story of C60 buckminsterfullerene (Figure 1) indicate that a specialized review is necessary and timely. The existence of the fullerenes as a family has now been established and it is useful to use a convenient nomenclature such as fullerene-60 or fullerene-70 which can apply to the whole family. There are of course numerous possible C<sub>60</sub> and C<sub>70</sub> cage isomers, however here we shall, in general, mean the most geodesically stable cages for which there is now no doubt in the case of the 60 and 70 atom species—they are  $(I_h)$  fullerene-60 and  $(D_{sh})$  fullerene-70 where standard symmetry labels have been added as prefixes. Since the existence of fullerene-60 and its spontaneous creation have ramifications in numerous areas from the properties of carbonaceous solids and microparticles through combustion, thermolysis, and synthetic organic chemistry to the nature of the carbonaceous constituents of space, these implications are also surveyed.

During a series of experiments in 1985 which probed the nature and chemical reactivity of the species produced during the nucleation of a carbon plasma the Co species was discovered to be stable by Kroto, Heath, O'Brien, Curl, and Smalley. It was proposed that this

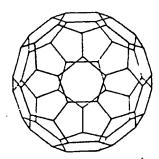


Harry Kroto (left) was educated at Sheffield University and after ds at the National Research Council, Canada (1964-1966). and Bell Telephone Laboratories (1966–1967) went to the Univ. ersity of Sussex where he is now Professor of Chemistry. His research into the production and spectroscopic characterization of new species such as the phospahaalkenes, phospahaalkynes; thocarbonyts, and polyynes led, via radioastronomy studies of aterstellar molecules, to carbon cluster beam experiments aimed terstellar molecules, to carbon cluster beam experiments aimed at understanding stellar chemistry. Wahab Altal (right) who was educated at Aleppo University (Syria) and Sussex University carrying out research on carbon clusters and laser chemistry. carrying our research on carbon customs and some reactions and Simon Balm (center) who is studying cluster beam reactions and astrophysical chemistry was educated at Durham University and Sussex University.

stability was due to geodesic and electronic properties inherent in the truncated icosahedral cage structure shown in Figure 1 and the molecule was named buckminsterfullerene. This novel proposal did not receive instant universal acceptance since it appeared to have been based on highly circumstantial evidence. Indeed it is now clear that there was a significant degree of scepticism in the minds of some with regard to the validity of the proposal, perhaps because the evidence was dispersed among many disparate scientific observations, much like the way that C60 itself may we now realize—be involved in many processes involving carbon in the environment and space. However, systems giving rise to C60 were subjected to many detailed investigations subsequent to the discovery paper,3 and some important points evolved which are worthy of highlighting:

(i) A wealth of convincing experimental evidence was amassed that showed that Ceo possessed unique physicochemical stability a conclusion totally independent of the cage structure proposal.

(ii) The fullerene cage proposal was the simplest and most elegant explanation of the unique behavior and no serious alternative explanation was ever presented.



91. NO 6

Figure 1. C<sub>50</sub> buckminsterfullerene

(iii) The proposal was consistent with many earlier observations on bulk carbon and clarified some previously unexplained phenomena in carbon chemistry.

The fullerene structural proposal has recently been confirmed by complementary observations from two groups. Krätschmer, Lamb, Fostiropoulos, and Huffman,4 in following up their earlier IR investigation (in 1989)5 which suggested that C<sub>60</sub> might be present in arc-processed graphite, extracted a soluble material which formed crystals. The X-ray analysis showed the material to consist of 10-A diameter spheroidal molecules and supplementary mass spectrometric and infrared data provided the first unequivocal evidence for  $C_{50}$  (and  $C_{70}$ ). In a parallel, independent investigation which probed this same original key observation,5 Taylor, Hare, Abdul-Sada, and Kroto found that similarly arc-processed graphite gave rise to a 720 mass peak, commensurate with the presence of fullerene-60, and that this material was soluble and could be extracted directly. The extracted C60 compound yielded a single 13C NMR line which proved that all 60 carbon atoms are equivalent as expected for the truncated icosahedral buckminsterfullerene structure. Taylor et al. also showed that  $C_{60}$  and  $C_{70}$  can be separated chromatographically and that the latter has the  $D_{5h}$ prolate, ellipsoidal structure first suggested by Heath et al.6 These results provide further support for the conjecture that a whole family of fullerenes exists. 7.8

Since these revelations, which are discussed further in section IX, the fullerene field has exploded and numerous groups are probing various facets of physicochemical properties of the fullerenes. Indeed a new field of carbon chemistry has been born, and the first faltering steps of the promising infant are described in section X. Thus this review is particularly timely as it is written at the precise moment when the final sentence in the last paragraph of the first chapter in the story of the fullerenes has been completed. The opening paragraphs in the next chapter are just being written and they herald a new era in which the flat world of polycyclic aromatic chemistry has been replaced by a postbuckmisterfullerene one in which round structures are favored under certain surprisingly common circumstances.10 This article reviews the buckminsterfullerene story from the time when it was just a twinkle in the eyes of a few imaginative theoreticians, through the experiments which revealed that it actually formed spontaneously and exhibited stability to the most recent revelations that it could be isolated and did indeed possess the round hollow cage structure as



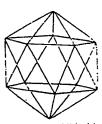


Figure 2. Diagram of Cop next to an icosahedron published in the book Aromaticity by Yoshida and Osawa. These authors discuss (in Japanese) the "superaromaticity" which might accompany electron delocalization over a three dimensional truncated icosahedral pure carbon molecule.

proposed. As many contributions to the story as could be traced by Dec 1990 are included.

# II. Summary of Relevant Carbon Studies Prior to the Discovery of $C_{\rm 50}$ Stability

At least part of the reason for the degree of interest engendered by the buckminsterfullerene proposal revolves around its high degree of symmetry. Mankind has always been fascinated by symmetric objects, indeed stone artifacts with the form of the Platonic solids. dating back to neolithic times, have been found in Scotland,11 indicating that human beings have long had a spiritual affinity with abstract symmetry and an aesthetic fascination for symmetric objects. The truncated icosahedron is one of the Archimedian semiregular solids; however in hollow form an early example appears in the book De Divina Proportione by Fra Lucia Pacioli. A reproduction of this drawing by Leonardo Da Vinci entitled "VCOSEDRON ABSCISVS VACVVS" is to be found in the book The Unknown Leonardo,12 which is rather more accessible than the original!

The C60 molecule itself was first suggested in a most imaginative and prescient paper by Osawa in 197013 and discussed further in a chapter on "Superaromaticity" in a book by Yoshida and Osawa14 in 1971; the original diagram is depicted in Figure 2. An equally imaginative article, which actually predates this work, was written in 1966 by Jones in which he conjectured on the possibility of making large hollow carbon cages. 15.16 The next paper was that of Bochvar and Gal pern in 1973 who also published a Hückel calculation on C<sub>60</sub> <sup>17,18</sup> In 1980 Davidson published a paper which used graph theory to deduce an algebraic solution of the Hückel calculation for fullerene 60.19 Davidson's orbital energy level diagram, depicted in Figure 3, was determined by using a calculator, and this paper contains an unusually prescient paragraph in the light of recent observations (particularly those in section VII): "Should such structures or higher homologs ever be rationally synthesized or obtained by pyrolytic routes from carbon polymers, they would be the first manifestations of authentic, discrete three-dimensional aromaticity. Haymet's study20 on this molecule coincided very closely with its discovery in 1985.3

On the experimental front there were many very important early papers on carbon clusters and these have already been reviewed. Perhaps the most interesting early carbon cluster papers (and the ones which in fact actually stimulated the discovery experiments) were

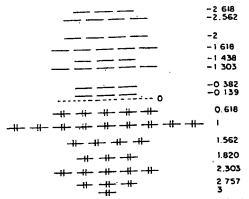


Figure 3. The Hückel molecular orbital calculation for buckminsterfullerene was carried out by Bochvar and Gal'pern<sup>17,18</sup> (1973) and Davidson<sup>19</sup> (1980), prior to, and by Haymet<sup>20</sup> (1985) coincidentally with, its discovery. The orbital energy level diagram (units of  $\beta$ ) depicted here is that published by Davidson<sup>19</sup> who determined it using graph theory to obtain simplified algebraic relations which were evaluated with a calculator (reprinted from ref 19; copyright 1981 Springer-Verlag Publishers).

those published by Hintenberger and co-workers in 1959 6321-24 in which it was shown that species with up to 33 carbon atoms could form in a carbon arc. The next important advance was made by Rohlfing, Cox. and Kaldor25 in 1984 who found that much larger carbon clusters ( $C_n$  with n = 30-190) could be produced by vaporization of graphite (Figure 4). Rohlfing et al. used the supersonic nozzle, laser vaporization technique developed by Smalley and co-workers at Rice University26 in 1981. In this technique clusters are made by laser vaporization of refractory materials into a pulse of helium or argon in the throat of a supersonic nozzle. The vaporized material nucleates in the gas pulse which then expands supersonically into a vacuum chamber where it cools and is skimmed. The skimmed beam passes into a second chamber where the entrained clusters are ionized by a second laser pulse and the cluster ion mass distributions determined by time of flight mass spectrometry (TOF-MS). The mass spectrum observed by Rohlfing et al.25 is shown in Figure 4; they pointed out that only ions with even numbers of carbon atoms were observable for the new family of clusters with more than 30 carbon atoms. Packing or magic number effects are very weak under these conditions.<sup>27</sup> Bloomfield et al.<sup>28</sup> also studied carbon clusters by the same technique and observed both positive and negative even numbered ions. They also studied the fragmentation behavior of the new family and in particular chose the C60 cluster for further study and showed that it could be photodecomposed with 532-nm multiphoton laser radiation.

# III. The Discovery of C<sub>50</sub>: Buckminsterfullerene

The state of the s

In September 1985 the reactions of carbon clusters were investigated by the Rice/Sussex group. 129,20 These experiments were aimed at simulating the conditions under which carbon nucleates in the atmospheres of cool N-type red giant stars. Circumstantial evidence

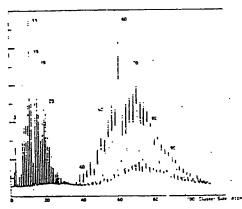


Figure 4. Time-of-flight mass spectrum, observed by Ronlifing, Cox and Kaldor, of carbon clusters produced by laser vaporization of graphite. In this experiment carbon clusters with 30-100 atoms were detected for the first time. These studies showed that only even-numbered clusters were stable reprinted from ref 25, copyright 1984 the American Institute of Physics.

sources of the long carbon chain molecules in the interstellar medium and in particular that the formation process might be related in some important way to soot formation. 31 The interstellar cyanopolymes (HC, N in = 5-11)) were discovered by a synergistic combination of laboratory microwave spectroscopy experiments. 33.34 theoretical analysis.35 and observational radioastronomy. 36-39 The cluster beam experiments showed convincingly that species such as HC-N and HC<sub>9</sub>N, which had been detected in space. <sup>36-38</sup> could be produced by such laboratory simulations of the conditions in carbon stars, 29,30 A second motivation for probing laser vaporization of graphite was the question of whether carbon clusters were associated with the so-called diffuse interstellar bands as Douglas had proposed in 1977.40 The development of resonant 2-photon ionization in conjunction with the cluster beam technique to obtain the high-resolution spectrum of SiC, by Michalopoulos et al.41 suggested that the electronic spectra of carbon clusters might be accessible by this technique. During the course of the experiments<sup>29,30</sup> which probed the behavior of the pure carbon clusters a striking discovery was made-under some clustering conditions the 720 mass peak appeared to be extremely strong (Figure 5). Indeed the intensity of the C60 peak, relative to the adjacent cluster distribution, could be varied dramatically just by altering the conditions. In particular, conditions could be found for which the mass spectrum was totally dominated by the C<sub>∞</sub> peak—at least in the mass range accessible (Figure 6). It was concluded that C<sub>80</sub> must be particularly stable to further nucleation and it was proposed that this might be explained by the geodesic factors inherent in a truncated icosahedral cage structure in which all the atoms were connected by  $sp^2$  bonds and the remaining 60  $\pi$  electrons distributed in such a way that aromatic character appeared highly likely.3

In these experiments it was found that the  $C_{70}$  peak also showed clear enhancement although to a lesser extent; the  $C_{60}/C_{70}$  ratio was ca. 5/1 in general. In previous experiments 25.27.25 the  $C_{60}/(C_{50}$  or  $C_{60}$ ) ratio was ca. 2/1 (Figure 4) whereas in the new experiments

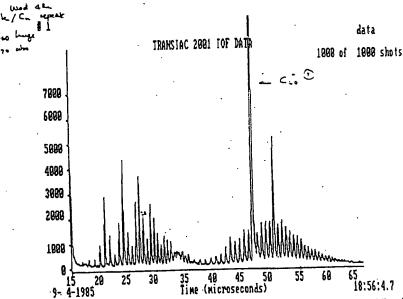


Figure 5. Time-of-flight mass spectrum of carbon clusters produced by laser vaporization of graphite (Sept 4, 1985) under conditions which first exhibited the dominance of the C<sub>60</sub> cluster and led to the recognition that 60 might be a "magic" number.

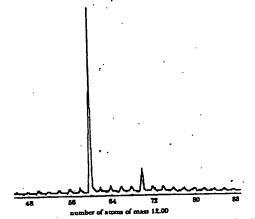


Figure 6. Time-of-flight mass spectrum carbon clusters produced by laser vaporization of graphite under the optimum conditions for observation of a dominant Co cluster signal.3 Note also the prominence of C70-

conditions were found in which a ratio of 20/1 or more was achieved (Figure 6). It was soon realized that although Ceo generally appeared fairly special, the conditions under which it appeared dominant were rather unusual. They were conditions in which the major fraction of the carbon had nucleated to form macroscopic particles too large to be detectable by the mass spectrometer. Thus it was recognized that the signal shown in Figure 6 shows the "small" carbon species which remain when the microparticles have formed. Due to the fact that geodesic structural concepts were a guide to the hollow cage structural explanation that

11 75 C.

د سے مرسون ندر سول جدیدل درسون مدیدن کی سدون دہ ہوں یہ دون سدیدن درسون در دون دو روز اور دو وارو ت خد دد (۱۵۱ بدار ۱۵۱ به ۱۵۱ به ۱۵۱ بدار ۱۵۱ بدار ۱۵۱ بدار ۱۱ بدار ۱۵۱ بدار ۱۵۱ د. د میت 36,35(54),39(31),40(48),41,46,49,52,32,34 7.39-tr

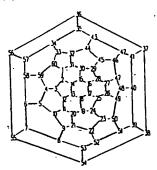


Figure 7. The IUPAC name of fullerene-60 determined by computer analysis—according to P. Rose. 47

cule was named after Buckminster Fuller, the inventor of the geodesic domes.<sup>43</sup> Although the name chosen, buckminsterfullerene<sup>3,44</sup> is a little long,<sup>45,45</sup> it is not as long as the IUPAC alternative and not as difficult to pronounce (Figure 7)<sup>47</sup> and certainly not as difficult to derive. \*\*28.49\* The name fullerene can be conveniently and appositely used for the whole family of closed carbon cages with the 12 pentagons and N (other than one) hexagons in an sp<sup>2</sup> network. \*\* For several reasons, not least the problem of ambiguity with international sports nomenclature, some other names are probably not as satisfactory; they are certainly less enlightening.
Since the buckminsterfullerene detection paper was

work has been carried out. Two complementary accounts covering many of the important general implications and experimental observations have been given by Kroto<sup>50</sup> and Curl and Smalley <sup>51</sup> More focused accounts have also been published dealing mainly with experimental observations. <sup>52-M</sup> astrophysical impirations, <sup>52-SS</sup> symmetry and structure considerations of fullerene-60, and the icosahedral giant fullerenes <sup>56</sup> The chemical implications have also been discussed by Kroto<sup>61</sup> and Kroto and Walton. <sup>10</sup> Hirota<sup>62</sup> and Heath<sup>63</sup> discuss fullerene-60 as well as other novel carbon molecules.

#### IV. Sources of C60

In the original work, which showed how conditions could be achieved to produce a signal in which the Coo peak was dominant, the pulsed nozzle/laser vaporization technique26 was used to produce the clusters from a graphite target and photoionization TOF-MS used to detect them. The laser-produced plasma expanded into a high pressure (ca. 1-10 atm) of He and the target graphite surface was continually replenished so that the surface remained essentially flat. A nozzle extender was used to increase the clustering time prior to expansion to ca. 100 µs and the high He pressure increased the nucleation rate. Although initially it was conjectured that perhaps graphitic sheet fragments might have been ablated from the graphite target and rearranged into the buckminsterfullerene structure, subsequent considerations suggested that C60 was more likely to have formed by nucleation from carbon vapor consisting, at least initially, of C atoms and very small carbon molecules.52 Negative ion distributions produced by crossing a laser with the cluster beam just as it exited the nozzle64 have been studied, and the relationship between these and positive and negative ion distributions. obtained directly from the vaporization zone (i.e. without photoionization), has been discussed by Hahn et al. 55 and O'Brien et al. 66 The consensus of opinion was that C60 appeared to exhibit special behavior whether charged (positive or negative) or neutral and that the nucleation rate order was neutrals > cations > anions.66 Very detailed discussion of the conditions under which C<sub>60</sub> appears to be special has been given by Cox et al.<sup>67</sup> These studies are discussed in more detail in section V.

Carbon cluster distributions exhibiting dominant Consignals, can be produced in another way as O'Keefe, Ross, and Baronavski<sup>68</sup> and Pradel et al.<sup>69</sup> have shown using high vacuum TOF-MS. In these experiments the graphite target is inside the mass spectrometer vacuum system and remains stationary. After several laser pulses a hole is drilled in the graphite and nucleation appears to occur in the cavity. McElvany et al., 10 using ICR-MS techniques, have shown that if the axis of the laser-drilled hole is aligned parallel to the trapping magnetic field a strong C<sub>50</sub>\* signal predominates in the mass spectrum. In a study of the small cluster distribution, McElvany, Dunlap, and O'Keefe<sup>71</sup> found that the vaporization of a diamond target produces the same distribution as does graphite. This result indicates that the clusters appear to be produced by nucleation of atomic/molecular carbon vapor rather by a process involving the ablation of bulk fragments from the target. Maijer and Rethine Thorse modified the mi

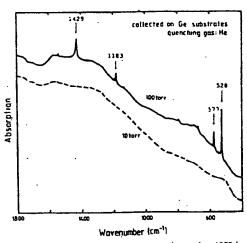


Figure 8. Infrared absorption spectrum observed in 1989 by Krätschmer, Fostiropoulos, and Huffmank from carbon produced by arc-discharge processing. Krätschmer et al. made the perceptive observation that the four sharp absorption features indicated might belong to fullerene-60. The frequencies were tantalizingly consistent with theoretical predictions (section VIII) for the fundamental vibrations of fullerene-60 treprinted from ref 74; copyright 1990 Elsevier Science Publishers.

vaporization procedure for producing  $C_{60}^{\ \ \ \ }$  in order to deposit material on a film. They have shown that the mass spectrum obtained by subsequent laser desorption of the resulting material yields a very similar cluster distribution to that of the cluster beam experiments. They have also carried out isotope scrambling measurements supporting the conclusion that  $C_{60}$  is assembled from small carbon species in the gas phase after vaporization (see section VI).

A fascinating and ultimately key observation was described in September 1989 by the Heidelberg/Tucson group: Krätschmer, Fostiropoulos, and Huffman<sup>5,74</sup> who detected four weak bands in the infrared spectrum of a film deposited from a carbon arc under argon (Figure 8). Krätschmer et al. pointed out that the vibrational frequencies of the four bands (and associated <sup>12</sup>C shifts) observed were in tantalizingly close agreement with theoretical estimates for fullerene-60 (details in sections VIII and IX).

Several other interesting studies have shown that laser vaporization of a wide variety of carbonaccous target materials (other than pure carbon) also yields a dominant C<sub>50</sub> signal: e.g. carbon films (Creasy and Brenna, <sup>76</sup> and Cambell et al. <sup>71-79</sup>), coal (Greenwood et al. <sup>50</sup>), polycyclic aromatic hydrocarbons (Giardini-Guidoni et al. <sup>51</sup> and Lineman et al. <sup>52,53</sup>). Last but not least, So and Wilkins <sup>56</sup> have shown that C<sub>50</sub> can be detected by laser desorption of soot! In fact they have observed even-numbered carbon clusters with as many as 600 carbon atoms (Figure 9). This result and similar experiments may indicate that giant fullerence may also be forming. <sup>50</sup> All experiments show that conditions can be found in which the C<sub>50</sub>\* peak is either prominent or dominant. However conditions also exist for which this is not the case. <sup>56</sup> It is likely that the availability of many other pathways to "organic" (H-containing species) may

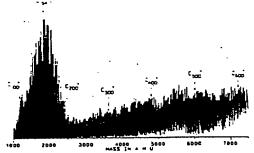


Figure 9. Laser desorption Fourier transform mass spectrum, observed by So and Wilkins, <sup>24</sup> of soot deposited on a KCl-coated stainless steel probe tip. Note that all the peaks here also correspond to even numbered carbon species. Since only even-numbered carbon aggregates can close perfectly it is possible that the explanation for this phenomenon is that these species are fullerenes and that the larger species are giant fullerenes of the kind depicted in Figure 22.

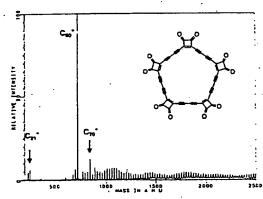


Figure 10. Remarkable positive-ion laser desorption Fourier transform mass spectrum, observed by Rubin et al., so of the ring carbon oxide depicted under low laser power. This oxide which might be expected to decarbonylate to yield a Commonocyclic ring has clearly dimersed to form Combinatorial lerene!

A most exciting result was described by Rubin et al. 85 who have used a combination of organic synthesis and laser desorption mass spectrometry. In a preliminary study by the same group (Diederich et al. 86) attempted to prepare pure carbon rings, a prominent peak for the C18 cluster was detected during mass spectrometric analysis of a laser desorbed 18-carbon ring precursor. This work has now been advanced in spectacular fashion; refined measurements on C<sub>18</sub> and C<sub>24</sub> precursors<sup>85</sup> yield mass spectra which show prominent  $C_{60}$  and  $C_{70}$ signals. However most striking is the observation that laser desorption of the C30 ring precursor produces a mass spectrum containing a totally dominant  $C_{00}$  signal! (Figure 10). This result suggests that, in the vapor phase, a spectacular dimerization process occurs in which two C<sub>30</sub> polyyne/cumulene rings combine in a concerted folding rearrangement to form the C<sub>80</sub> cage. 10 The implications of this process and indeed other aspects of the fullerene discovery for organic chemistry have been considered. 10.61

医人名西特特

Some of the most important of all these experiments were those of Homann and co-workers<sup>87-90</sup> who detected

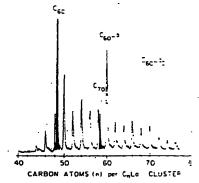


Figure 11. Mass spectrum of C<sub>a</sub>La cluster complexes and bare C<sub>a</sub> clusters as observed by Heath et al. when LaCl-doped graphue is leser vaporized (ArF 6.5 eV. 10 mJ cm<sup>2</sup>). Note the perucularly strong peak for C<sub>m</sub>La and the absence of a peak for C<sub>m</sub>La. This result is discussed in section VI tadapted from ref.

 $C_{60}^{\star}$  in a sooting flame. These observations are discussed in more detail in section VII.

#### V. Stability and Intrinsic Properties of C<sub>50</sub>

After the buckminsterfullerene structure was proposed3 the intrinsic properties of the species were probed by the Rice/Sussex group. 50-54 It was clearly vital to determine how reliable the experimental observation of the "stability" of the C60 cluster was, i.e. how "special" or "magic" the cluster actually was and how certain one could be about the buckminsterfullerene hollow cage explanation. After all, the proposal appeared to rest entirely on the observation of a single. strong mass spectrum peak at 720 amu (Figures 5 and 6), and such highly circumstantial evidence needed further support. Mass spectrometry is particularly susceptible to erroneous conclusions drawn on the basis of magic numbers due to the likely presence of ionization and fragmentation artifacts. Various aspects of the original experiment led to the conclusion that the cation mass spectrum (Figures 5 and 6) was most probably an accurate reflection of the neutral cluster distribution. Nevertheless it was necessary to carry out experiments in order to probe the behavior of C60 more deeply in order to generate further evidence; albeit still circumstantial, to support the stability conclusion and the cage structure proposal.

During the period from 1985 to 1990 many experiments were performed by a number of groups operating in the cluster field which probed carbon behavior with a view to confirming or falsifying the fullerene-60 proposal. If C<sub>80</sub> really were a cage then the most obvious next step was to attempt to trap an atom inside the cage. The first result, in this context, was the observation of CeoLa by Heath et al. By using a graphite disk, soaked in LaCl, solution a strong signal was obtained for the monolanthanum complex Coola, with no evidence of a peak for C<sub>60</sub>La<sub>2</sub> (Figure 11). Cox et al.<sup>31</sup> questioned the conclusion. They pointed out that, since Conneeds two 6.4 eV (ArF) photons for ionization and Cools only one, the relative strengths of the Cools and bare C<sub>80</sub> MS signals should not necessarily be taken as reliable gauges of their respective abundances, and a possible CanLas+ signal might be too weak to detect

. . :

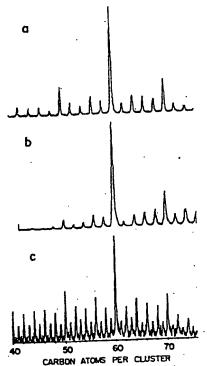


Figure 12. Carbon cluster ions observed under various production Figure 12. Carbon cluster ions observed under various produced conditions. (a) negative ions produced by directing a KrF eximer into the nozzle during expansion, (b) positive carbon cluster ions produced directly during vaporization in the nozzle without the sid of the KrF eximer laser, and (c) negative ions produced the sid of the KrF eximer laser, and (c) negative ions produced the sid of the KrF eximer laser, and (c) negative ions produced the sid of the KrF eximer laser, and (c) negative ions produced the sid of the KrF eximer laser, and (c) negative ions produced the sid of the KrF eximer laser, and (c) negative ions produced the sid of the KrF eximer laser, and (c) negative ions produced the sid of the KrF eximer laser, and (c) negative ions produced the sid of the KrF eximer laser. directly during vaporization in the nozzle, again without the aid of the KrF excimer laser but with longer residence time in the clustering region than in the case of the positive ions depicted in b (reprinted from ref 52; copyright 1987 Gordon and Breach Science Publishers, Inc.).

Cox et al. 57 have discussed further the cage hypothesis in general and metal atom encapsulation in particular and after detailed assessment they conclude that overall their observations are non-committal over whether  $C_{\Theta}$ was a cage or not

For the smaller carbon species the positive ions display the well known magic numbers: 11, 15, 19, 23 (the so-called "An = 4" effect, cf. Figure 4) whereas the negative ions exhibit a different sequence.21-2413 The paper announcing the original discovery assumed that the mass spectra (Figures 5 and 6) reflected accurately neutral carbon cluster distributions. If the buckminsterfullerene structural proposal were correct however, the positive and negative ion distributions would be expected to exhibit a similar prominence for the 60-carbon atom analogue. The first experiment to probe this possibility showed that negative ions, produced by laser ionization just after the cluster beam exited from the nozzle exhibited an anion mass spectrum in which Ceo was dominant. In this experiment the neutral species became negatively charged by electron transfer. If the positive or negative ions, produced directly by vaporization are studied, it is found that only after clustering is allowed to continue for a

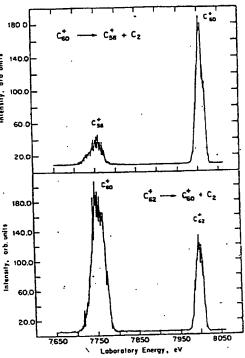


Figure 13. Metastable mass-analyzed ion kinetic energy scans (MIKES) published by Radi et al.<sup>23</sup> The parent ion (on the right) is mass selected by the magnetic analyzer and the horizontal axis is a scan of the electrostatic analyzer voltage. The parent ion energy is 8 keV. C<sub>1</sub> loss is observed from C<sub>10</sub> (above) and C<sub>11</sub> (below). Note the dramatic differences in metastable activity as reflected by the relative intensities of the product peaks, relative to their parent ions in these two cases (reprinted from ref 93; copyright 1990 the American Institute of Physics).

significant length of time is the C<sub>60</sub> anion dominant<sup>66</sup> otherwise it is not. Some examples of mass spectra recorded under various conditions 11.54.55 are presented in Figure 12. Cox, Reichmann, and Kaldorsi describe some intriguing relative time-of-flight differences in behavior between various individual clusters, in particular C<sub>28</sub> and C<sub>60</sub>, which are highly dependent on the nozzle parameters. These experiments appear to suggest that wall reactions may occur in the nucleation channel. It is possible that what was observed in this experiment was Ceo deposited in the channel which subsequently desorbed. The main evidence for the importance of wall effects lies in the detection of Cook clusters when a new, pure (i.e. K free) carbon target replaces a previous one doped with potassium.

Important observations have had a bearing on the stability of C<sub>60</sub>. The very early experiments by Bloomfield et al. 25 showed that C<sub>60</sub> was susceptible to multiphoton fragmentation. A series of studies by Bowers and co-workers showed that Coc could undergo metastable fragmentation. Particularly interesting is the observation that C<sub>so</sub> exhibits much lower metastability than other neighboring clusters such as C<sub>so</sub> as shown in Figure 13. These results suggest that hot Coo may exhibit phenomena associated with fluidity perhaps an intriguing form of surface fluidity. On the

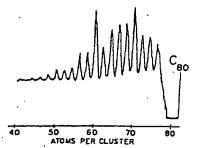


Figure 14. Fragmentation products under ArF (15 mJ cm $^{-2}$ ) irradiation observed by O'Brien et al. <sup>35</sup> Under irradiation the mass selected  $C_{m}^{*}$  cluster (including ca. 20%  $C_{70}$  and ca. 10%  $C_{20}$ ) is here seen to fragment into smaller even clusters:  $C_{70}$ , etc. by loss of  $C_{70}$   $C_{40}$ , etc. Particularly interesting is the observation that  $C_{20}$  and  $C_{70}$  are favored fragmentation products (reprinted from ref 95; copyright 1988 the American Institute of Physics).

Figure 15. Hypothetical fragmentation-rearrangement mechanism presented by O'Brien et al., involving C<sub>2</sub> loss and cage re-sealing which could explain the fragmentation phenomena in Figure 14 (reprinted from ref 95; copyright 1988 the American Institute of Physics).

other hand, O'Brien et al.95 and Weiss et al.96 have shown that cold Co exhibits little, if any, evidence for fragmentation. The likely explanation for this disparity is that clusters produced under the vacuum vaporiza-tion conditions<sup>22,97-94</sup> possess massive amounts of internal energy leading to metastable C<sub>50</sub><sup>+</sup>. As special behavior is most dramatic after extensive degrees of nucleation have occurred it is possible that the Co signal observed under vacuum ablation conditions is actually a mixture of isomers, at least in part. Related studies by Hasselberger et al. 78 show that metastable fragmentation is less severe when clusters are produced with lower internal energies. The measurements of O'Brien et al. showed that multiphoton fragmentation of clusters with 32-80 atoms occurred by elimination of even carbon fragments,  $C_n$  ( $n=2,4,6,\ldots$ ), rather than lower energy  $C_2$  species. Particularly intriguing is the observation that large clusters, with 70 or more atoms fragment to form smaller even-cluster distributions in which Ceo is special (Figure 14). Clusters with less than 32 atoms fragment into a range of smaller carbon species, a result interpreted as evidence that clusters with less than 32 atoms were not cages. O'Brien et al. 95 also presented an interesting mechanism for this process which is depicted in Figure 15. Laser irradiation studies by Weiss et al. 88 showed that the metal complexes were also quite resistant to photofragmentation. They also showed that multiphoton fragmentation of C<sub>80</sub>M<sup>+</sup> resulted in metal-complex products  $C_nM^+$  for which the critical smallest sizes occur at n =48, 44, 44-42 for M = Ca, K, and La, respectively (Figure 16). This result provided strong circumstantial evidence for metal atom encapsulation because the minimum physical cage size scales with the ionic radius



Figure 18. High-order photofragmentation pattern of C<sub>50</sub>K\* (above) and C<sub>60</sub>Ca\* (below) detected by FT-ICR mass spectrometry by Weiss et al. \*\* The break-offs observed at C<sub>60</sub>Cs\* and C<sub>44</sub>K\* are in excellent agreement with expectation for the smallest fullerene networks capable of encapsulating the metals, based on the known ionic radii (reprinted from ref 96; copyright 1986 American Chemical Society).

#### of the metals in the series.

Prior to the isolation of macroscopic samples of the fullerenes (section IX) several experiments were carried out in order to determine their physical, mainly spectroscopic, properties. Tandem TOF-MS experiments were devised to explore the possibility that the spectra of  $C_{60}$  (neutral) and  $C_{60}^+$  (the positive ion) might be responsible for the astrophysically intriguing diffuse interstellar bands (section XI). These experiments involved the resonant photodissociation of a van der Waals complex of benzene with neutral  $C_{60}$  and  $C_{60}^+$ . It proved possible to photofragment  $C_{60}$ - $C_6$ - $H_6$  but not the ion complex,  $C_{50}$ - $C_6$ - $H_6$ , probably because charge transfer forces bind the adduct too tightly in the ion complex. Yery weak photofragmentation of the neutral complexes of  $C_{60}$  with  $C_6$ - $H_6$  and  $C_{12}$ - $C_{12}$  was observed at 3860 Å by depletion spectroscopy.

Yang et al. 39 used an ingenious technique developed by Cheshnovsky et al. 100 to observe the UV photoelectron spectra of negative cluster ions. In these experiments the spectra of carbon clusters from C<sub>48</sub> to C<sub>M</sub> have been observed. Of particular interest are the UPS patterns of C<sub>80</sub>, C<sub>80</sub>, and C<sub>70</sub> which show a low energy LUMO feature consistent with closed shells for the neutral species. Con had the lowest electron affinity: viz 26-28 eV. These observations provided further strong support for the fullerene proposal. The ionization potential of C<sub>60</sub> was obtained in an elegant way by Zimmerman et al.<sup>101,102</sup> who used a series of charge transfer measurements with various reactants of known IP to bracket the IP of  $C_{80}$ : 7.61  $\pm$  0.11 eV. This result was consistent with conclusions drawn from early experiments which indicated that the IP lay between the energy of the ArF excimer laser (6.4 eV) and that of the F. laser (7.9 eV) hecsina C., was 9-nhaten i

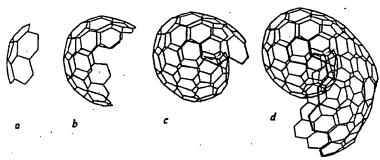


Figure 17. Diagramatic representation 108 of a hypothetical carbon vapor nucleation scheme ed for the formation of concentric Figure 17. Diagramatic representation of a hypothetical carbon vapor nucleation scheme proposed for the formation of concentric shell graphite microparticles. Note that the structure c has overlapped and so trapped the trailing edge inside the spiraling network. This species is thus essentially the embryo for further growth. It is proposed that C<sub>50</sub> might be produced by a modification of this process in which the edges meet and seal to form a closed cage. In such a case further growth by chemical bond formation might be expected to be halted. It was conjectured that similar structures might occur as intermediates during soot nucleation (reprinted from ref 108; copyright 1988 Macmillan Magazines Ltd.).

ArF and 1-photon ionized by F<sub>2-103,67</sub>
As mentioned in section IV, the most intriguing and convincing spectra were those obtained in the infrared study of Krauschmer, Fostiropoulos, and Huffman in 1990<sup>5,74</sup> (see further details in sections VIII and IX).

### VI. Reaction Studies

的现在分词美国

÷.;

The first reaction studies aimed at probing the cage concept were those of Heath et al. and Cox et al. 91,67 (discussed in section V) who studied the carbon/metal complexes. Rohlfing et al.25 and Heath et al.29.30 carried out similar reaction studies which focused mainly on the properties of the carbon chains. It is also important to note that van der Waals complexes can form in the

supersonic beam if C60 is cold. When various gases such as CO, NO, and SO<sub>2</sub> were introduced into a reactor, placed downstream from the nozzle in which C60 is formed, Zhang et al. 103 showed that all the even carbon clusters were totally unreactive. The odd clusters were, on the other hand, very reactive. These experiments gained significant further support from the studies of McElvany et al. 70 and Weiss et al. 86 which showed C60 and its analogues to be extremely unreactive in an ICR trap. However if gases are mixed with the driver gas in the nozzle, reactions can take place before and after Ce is formed. With hydrogen, a wide range of hydrocarbon products is detected (Rohlfing, 104 Hallett et al., 106 and Doverstal et al. 106). Rohlfing has used an in-line reflection modification of the cluster beam technique and made some very careful high-resolution mass spectrometric measurements of the reactions of clusters C20-C80 with hydrogen.104 The variations in reactivity appear to be structure related and consistent with the cage proposal. The study suggests that chain cluster species with as many as 44 carbon atoms may be present. Complementary experiments by Hallett et al. 105 and Doverstal et al. 105 indicate that clusters in the C<sub>20</sub> C<sub>40</sub> range show at least three different types of reactivity as evidenced by the mass spectrometric patterns of the hydrogenated products. The observations 106 are consistent with the proposal that small fullerenes (C20, C34, C22, C32, C50) can form. They are also consistent with the fact that formation that no 22 atom fullerene can exist, as

### VII. Gas-Phase Carbon Nucleation and C60 Formation

It would appear that most workers in the field are able to observe special behavior fairly easily and under a wide range of conditions, all of which have one major feature in common: C60 appears to be dominant only when nucleation nears completion, leaving behind C60 and other even-numbered relatives such as C70. This result has one obviously simple explanation; at least some fraction of the even clusters—particularly  $C_{60}$ —is unreactive toward growth into macroscopic particles. The spontaneous creation of Co requires a mechanistic explanation. In particular, entropy factors clearly need to be carefully assessed when it is proposed that so symmetric an object is formed in a chaotic plasma. A feasible nucleation mechanism was provided by Zhang et al. 100 and refined further by Kroto and McKay. 108 The nucleation model proposes that curved sp²-linked (aromatic) carbon networks form (Figure 17) and can serve as embryos for further growth. The energetics of sheet carbon cluster radicals is invoked to explain the curvature/partial closure. Essentially the drive toward closure is governed by the energy released as a result of eliminating the edge dangling bonds. For instance a flat graphite-like sheet of 60 atoms would have at least 20 dangling bonds, whereas fullerene-60 would, of course, have none. In general, in a chaotic system, partly closed, overlapped embryos, such as that shown in Figure 16c, are expected to form and which, once overlapped, cannot close perfectly. These species are probably highly active nucleation sites to which permanent chemical binding of adsorbing fragments can take place. Of course some form of closure/annealing process might take place if the temperature is high enough for intra and extra network rearrangement to occur. It was proposed 103,106 that during this general spiral nucleation process some embryos would close forming fullerenes, particularly fullerene-60 which would no longer present a site for efficient accretion. The process is primarily a physicochemical nucleation scheme in which the fullerenes act as deadends for the most rapid nucleation.

After embryo formation, epitaxial growth has been shown to result in icospiral graphitic giant molecules or microparticles 108 with structures consistent with

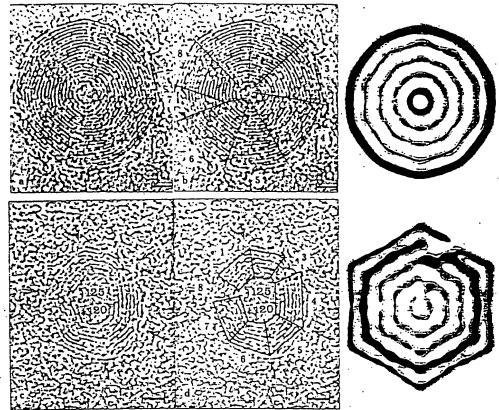


Figure 18. Comparison by McKay et al. 111,112 between TEM images of polyhedral graphitic microparticles observed by lijima 100 and Figure 18. Comparison by McKay et al. "So between 12.11 images of polyhedral graphitic microparticles observed by lijima and simulated TEM images for a hypothetical spiral shell particle predicted by the nucleation scheme depicted in Figure 17. The fairly round particle observed by lijima which is depicted in a and b is seen to exhibit a similar pattern to the simulation top right. On the other hand the more polygonal particle, shown in c and d, exhibits a similar pattern to the simulation shown bottom right. The simulations are for the same particle observed from different angles. The hypothetical particle has shell interconnections which can most easily be seen in the lower right simulation. In b and d the polygonal outlines are delineated.

those of spheroidal graphitic microparticles observed by Iijima in 1980.<sup>109,110</sup> Kroto et al. <sup>111,112</sup> have provided further support for the scheme in the form of TEM image simulations based on the icospiral concentric shell structure concept, 108 in excellent agreement with the Iijima images as depicted in Figure 18. Roulston et al. 113 have shown that certain electronic and structural properties of amorphous semiconducting carbons can be explained on the basis of a spheroidal graphitic infrastructure, rather than by the traditional flat mi-crostructure. Yacaman et al. 114.115 have shown that FT power-spectra processed, electron microscope images of carbon microparticles appear to be consistent with the quasiicosahedral spiral substructure. 108 Attention has been drawn to the fact that small graphitic microparticles actually consist of crystalline quasiicosahedral graphitic cores surrounded by amorphous carbon surface layers. 118,109 Interestingly, Lijima 110 has shown that the TEM structure at the nucleus of one of the carbon microparticles, studied earlier 100 was consistent with the image expected if it were a Coo cage. With hindsight this result demands further serious investigation to see whether fullerene-60 can itself be encapsulated during

later stages of particle growth.
Wales<sup>117</sup> has considered some statistical aspects of the growth dynamics of closed-cage structures and Bernholc and Phillips have discussed the kinetic factors involved in the growth of carbon clusters in general. 118

It was also suggested that a modified form of the nucleation scheme, devised to account for the spontaneous creation of C<sub>69</sub>, could also explain the spheroidal nature of soot. 103,108,5051,119 This proposal was criticized by Frenklach, Ebert, and co-workers 120-123 who favor an earlier theory, which invokes the physical condensation of flat PAH molecules held together by van der Waals forces into coagulating liquid drops. However, Harris and Weiner point out how little has been firmly established about the soot formation mechanism.<sup>124</sup> It can in fact be demonstrated<sup>125</sup> that the new scheme is broadly consistent with kinetic, structural, and chemical observations made on soot and its formation process.

The new nucleation scheme predicts that some C<sub>50</sub> should form as a byproduct<sup>102,106</sup> of soot production. Subsequently Gerhardt, Löffler and Homann, 87-90 in studies of the ions produced in a sooting flame, found conditions under which the mass spectrum shown in

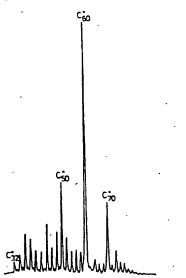


Figure 19. Mass spectrum, observed by Gerhardt, Löffler, and Homann. 57-60 of positive ions produced by a sooting benzene oxygen flame (C/O = 0.76) (reprinted from ref 87; copyright 1987 Elsevier Science Publishers).

Figure 19 is obtained. This spectrum is almost identical with that observed during the pure carbon laser vaporization experiments where  $C_{60}^+$  is the dominant ion! Homann and co-workers conclude that this observation should not be taken as support for the new spiral nucleation scenario as the tell-tale even ions with a dominant  $C_{60}^+$  peak are not seen until after the inception of soot particle formation. The carbon/hydrogen reaction studies  $^{104-105}$  promise to shed further light on the soot formation process, but the way in which the results might dovetail with the conventional data remains to be ascertained. Kroto has summarized the present state of affairs from this viewpoint.  $^{125}$ 

## VIII. Theoretical Studies of the Fullerenes

Theoretical studies predating the discovery of C<sub>60</sub> have been discussed in section II. After the discovery, theoreticians had a ball and many aspects of the molecule's properties have already been probed. The comprehensive overview of theoretical work on fullerene-60 presented by Weltner and Van Zee² is here conflated with more recent work.

One important aspect of the original experimental observations was the fact that  $C_{70}$  also showed special

behavior. Topological and chemical stability arguments, as discussed by Krotos and Schmalz et al., explain this observation as being entirely consistent with the fullerene proposal. Indeed these studies suggested that if the C60 mass spectrometric signal were due to its having a closed cage fullerene structure. C-, should show special behavior also, for the same reason. Thus most importantly and rather convincingly, the fullerene structure proposal no longer rested on the single line observation. In fact it had now gained significant further support by the fact that a prediction had heer. made and neatly confirmed. Indeed the two observations, taken together, provided convincing evidence for the existence of a whole family of fullerenes and further probing suggested that in addition to  $C_{60}$  and  $C_{-0}$ , the C24, C28, C32, and C50 clusters (Figure 20) should also show varying degrees of special stability<sup>8,9</sup> (N.B. fuilerene-22 cannot exist<sup>107</sup>).

The dominance of  $C_{60}$  and  $C_{70}$  was ascribed to the fact that these are the smallest fullerenes that can have an isomer (one in each case) in which none of the 12 pentagonal configurations, necessary and sufficient for closure, abut. 8.9 It was shown 8.50 that the predictions were commensurate with the mass spectrum obtained by Cox et al. 87 (Figure 21) and consequently there existed convincing experimental evidence for the fullerene family proposal. Since even-numbered carbon clusters are detectable with as many as 600 or more carbon atoms, 80 the possibility of giant fullerenes 108.125 such as  $C_{240}$  and  $C_{540}$  shown in Figure 22 appears to be an exciting possibility. 60

Isomer stability has been discussed by Stone and Wales<sup>121</sup> who noted that the difference in energy between isomers is small and suggested that the C<sub>50</sub> signal should be due to a mixture of isomers. This result is difficult to reconcile with the observation (Figures 5 and 6) since it leads to the conclusion that C<sub>50</sub> is no more special than other clusters such as C<sub>52</sub>. Potential energy functions have now been developed for the carbon cages systems by Takai et al. <sup>128</sup> and Balm et al. <sup>129</sup> The simulated annealing, Monte-Carlo methods used by Zerbettol<sup>30</sup> to study the behavior of small carbon clusters have been applied by Ballone and Milani<sup>31</sup> in order to show that the fullerene cages are minimum energy structures.

A group theoretical analysis of the electronic properties of the fullerene family, by Fowler and Steer. <sup>107</sup> showed that the members,  $C_n$  where n=60+6k (k=0,2,3,4,..., i.e. an integer other than one), should have closed-shell electronic structures. The degree of aromaticity in a compound is of interest, and the number of Kekulë structures is often considered to be a guide. A total of 12 500 for fullerene-60 has been calculated

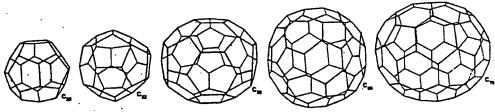


Figure 20. Five possible "magic" fullerenes predicted to display enhanced stability, relative to others in the range with 20-80 atoms, on the basis of chemical and sendesic factors (reprinted from set 8: committee 1087 Macmillan Marsaines 1 ed )

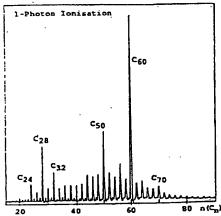


Figure 21. Time-of-flight mass spectrum taken from the data of Cox. Reichmann, and Kaldor. The strong peaks are in excellent agreement with expectation if they correspond to fullerenes. The fullerenes 24, 28, 32, 50, 60, and 70 (Figure 20) are predicted to exhibit enhanced stability, i.e. are magic. Note the sharp cutoff at  $C_{24}$  which is consistent with the fact that a no  $2^{\circ}$  atom fullerene can form.

by Schmalz et al.. <sup>132</sup> Hosoya, <sup>133</sup> Brendsdal and Cyvin, <sup>134</sup> and by Elser. <sup>135</sup> Resonance circuit theory has been applied to this problem by Schmalz et al., <sup>132,9</sup> Klein et al., <sup>136,137</sup> as well as Randic, Nikolic, and Trinajstic. <sup>138,140</sup> These studies indicate that account must be taken of the fact that some resonance structures make negative contributions to the aromatic stabilization. Schmalz et al. <sup>9</sup> compared resonance circuit theory with Hückel molecular orbital (HMO) theory and concluded that C<sub>60</sub> should be less aromatic than benzene. Amic and Trinajstic. <sup>140</sup> discuss stabilization arising from bond delocalization. Graph theory has been applied to C<sub>60</sub> and to other systems by Balasubramanian and Liu <sup>141,142</sup> and also by Dias who has circumvented group theory in order to simplify Hückel calculations. <sup>143</sup> Hückel calculations on fullerene-60 have been made by Haymet <sup>144,25</sup> and the stabilization due to delocalization discussed. Jiang and Zhang <sup>145</sup> have calculated the stability of fullerene-60 by Hückel theory using moment analysis techniques. Hess and Schaad <sup>146</sup> as well as

Aihara and Hosoya 147 have also applied Hückel theory to the problem, focusing on aspects of spheroidal aromaticity.

Fowler and Woolrich 148 have made three-dimensional HMO calculations which predict that C<sub>60</sub> and C<sub>70</sub> are closed shell systems. Fowler 148 extended this approach in order to assess the stability in other, larger fullerene cages, while Fowler, Cremona, and Steer 150 have discussed bonding in nonicosahedral spheroidal fullerene cages. Fowler 151 has extended these ideas to various classes of cylindrical fullerenes and predicted closed electronic shells with an empty nonbonding orbital for clusters consisting of 10(7 + 3k) and 12(7 + 3k) atoms with 5- and 6-fold symmetry. Ceulemans and Fowler 152:153 considered possible Jahn-Teller distortion pathways for icosahedral molecules.

Byers Brown<sup>154</sup> has discussed the simplification that high symmetry imparts to π-system calculations and obtained algebraic solutions for the orbital energies of fullerene-60. Electronic and vibrational properties were calculated by using a two-dimensional HMO method by Coulombeau and Rassat.<sup>155</sup> Semiempirical calculations including the effects of nonplanar π-orbital overlap due to curvature have also been carried out by using the free-electron model in the Coulson-Golubiewski, self-consistent Hückel approximation by Ozaki and Takahashi.<sup>156</sup> Haddon et al.<sup>157,156</sup> have also considered the effects of nonplanarity, i.e. pyramidalization.

Extended Hückel calculations by Bochvar, Gal'pern, and Stankevich<sup>159</sup> and INDO and INDO/CI calculations by Feng et al. <sup>160</sup> have been applied to C<sub>60</sub> and its isomers. A comparison between C<sub>60</sub> and graphite was made by MNDO with geometry optimization by Newton and Stanton. <sup>161</sup> McKee and Herndon <sup>162</sup> also applied MNDO theory to cage carbons and concluded that the flat "graphitene" cage, <sup>144</sup> in which two coronene sheets are linked by pentagonal rings at the edge to form a disk-like structure should be more stable then fullerene-60. These authors also considered the mechanism of formation arising from rearrangement. Rehybridization and bonding were studied by Haddon, Brus, and Raghavachari who applied the x-orbital axis vector/3d-HMO (POAV/3D HMO) method <sup>157,158</sup> and concluded that larger clusters were favored. It was also postulated that fullerene-240 should be more stable than C<sub>60</sub>. Lüthi and Almlöf<sup>163–165</sup> have carried out

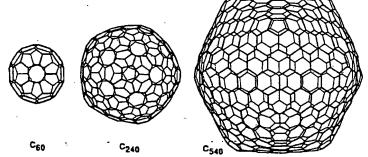


Figure 22. The set of fullerenes C<sub>20</sub>, C<sub>240</sub>, and C<sub>240</sub> with diameters in the ratio 1:2:3. Kroto and McKay<sup>108</sup> showed that quasiicosahedral shape develops rapidly for the giant fullerenes. Strain in the giant fullerenes is expected to be focused in the regions of the corannulene-like cusps. The surface thus becomes a smoothly curving network connecting the twelve cusps (reprinted from ref 108; copyright 1988 Macmillan Magazines Ltd.).

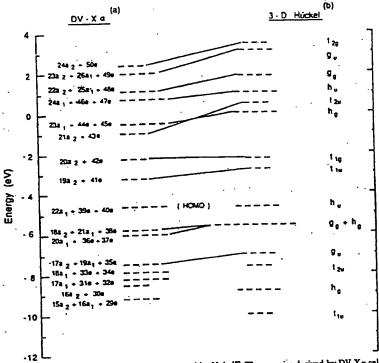


Figure 23. Orbital energy level diagram for fullerene-60 presented by Hale. <sup>169</sup> The energies derived by DV-X $\alpha$  calculations assuming  $D_3$  symmetry on the left are compared with Hückel results. In the diagram  $\beta$  has been given the value -2.52 eV (reprinted from ref 169; copyright 1986 American Chemical Society).

large-scale restricted Hartree-Fock calculations and they deduced that  $\Delta H_{\rm f} = 415$ –490 kcal/mol (relative to graphite) the electron affinity should be 0.8 eV and the ionization energy 7.92 eV. The electron affinity (2.4 eV) has been calculated by Larsson, Volesov, and Rosen<sup>165</sup> and by Braga et al. <sup>167</sup> Schulman and Disch<sup>168</sup> have calculated the heat of formation on the basis of ab initio SCF theory.

Hale determined electronic properties, such as the ionization energy for fullerene-60, by the discrete variational (DV)-Xa method using the Slater transition state formalism. Such calculations tend to be good for spheroidal systems. Hale's orbital energy level diagram for fullerene-60 is reproduced in Figure 23. The linear combination of muffin-tin orbital method in its atomic sphere approximation (LMTO ASA) was applied by Satpathy. To Calculations in which the partial retention of differential overlap PRDDO approach was applied were carried out by Marynick and Estreicher. 171 Stone's tensor surface harmonic theory was used by Fowler and Woolrich. 148 The IMOA method (iterative maximum overlap approximation) was applied to a range of fullerenes by Kovacević, Graovac, and Babic<sup>172</sup> to assess hybridization, structure and the amount of strain in these cages. Haddon 178 has discussed degree of pyramidalization considerations for fullerene-60 and other 

Fabre and Rassat have reviewed the properties of mown aromatic molecules which are essentially com-

In some of the calculations the electronic spectra of the fullerenes were the main focus. The calculations of Kataoka and Nakajima<sup>178</sup> and László and Udvardi<sup>178</sup> used the Pariser-Parr-Pople method (with CI) to determine spectra, structural parameters, and oscillator strengths. Optimized INDO calculations were published by Shibuya and Yoshitani. The electronic structure and the spectra have also been studied by the CNDO/S method (including CI) by Larsson et al. Sand by Braga et al. Hayden and Mele. See and by Braga et al. Hayden and Mele. See and by Braga et al. Hayden and Mele. See and by Braga et al. See and by Serie, Orlandi, and Zerbetto<sup>179</sup> who have also estimated Franck-Condon patterns and phosphorescence quantum yields.

Several calculations focused on the vibrational properties of fullerene-60. The result of primary (and historical) significance is that only four fundamentals are IR active due to the high symmetry of the molecule. Of the 174 vibrational modes giving rise to 42 fundamentals of various symmetries, four have t<sub>10</sub> symmetry and are IR active whereas 10 (eight h<sub>e</sub> and two a<sub>p</sub>) are Reman active.

Newton and Stanton are gave preliminary details of the vibrational behavior of fullerene-60 using MNDO theory. A non-Cartesian coordinate method was employed to describe the Cartesian coordinate method was employed to describe the Cartesian and George 180 Ah initio

SCF/STO-3G calculations of the vibrational properties of C<sub>50</sub> and other symmetric carbon cages have been published by Disch and Schulman <sup>181</sup> Schulman et al. <sup>182</sup> have applied the ab initio and AMI methods to fullerene-24 and fullerene-60 in order to obtain heats of formation, vibrational frequencies, and ionization energies. Coulombeau and Rassat have considered the vibrations of several fullerenes up to fullerene-120.183 They have also discussed hydrofullerenes. 184 In addition to calculating the rotational properties on the basis of icosahedral symmetry analysis, <sup>184</sup> Weeks and Harter have carried out a normal mode study on the basis of a classical spring/mass model. 185 They have also discussed the rovibrational properties of fullerene-60. 185-189
Stanton and Newton 190 extended and revised earlier MNDO studies giving detailed information on the normal modes. They have derived group theory invariance theorems for vibrational analysis and have discussed the Au vibration which essentially consists of rotary oscillations of the pentagonal rings. Cyvin et al. 191 used a 5-parameter force field to calculate the frequencies of the four IR active and 10 Raman-active modes; and Brendsdal et al. 192 have considered approximate methods in order to determine all 46 vibrational frequencies. Brendsdal<sup>153</sup> has discussed the symmetry coordinates.

Slanina et al. have carried out a harmonic vibrational analysis within the AM1 method for fullerene-60 and also fullerene-70.<sup>194</sup> The study has been extended to include consideration of structural, energetic, and thermodynamic properties of both species using MMP2 and MNDO methods. <sup>195-197</sup> Bakowies and Thiell<sup>198,198</sup> have used the MNDO approach to calculate the IR spectra of a whole range of fullerenes from C<sub>24</sub>-C<sub>240</sub>. For C<sub>70</sub> they deduce that one vibrational band should be significantly more intense than the rest, see section X.

Heymann has discussed the possibility that He may be trapped in a fullerene-60 cage.200 Calculations have been made of the spectroscopic properties of various intracage complexes by Ballester et al.201 assuming the central atom is trapped in a polarizable uniform (spherical) dielectric cage. Kroto and Jura<sup>202</sup> have discussed the importance of charge-transfer processes in the spectra of neutral and ionic fullerene intra- as well as extracage (van der Waals) complexes. For the ions the energy is just the difference between the ionization potentials of the  $C_{00}$  cage and the encapsulated species. Van der Waals complexes such as Co. H+ are likely to be particularly important (section XI). Rosen and Waestberg have calculated the electronic structure of C<sub>50</sub>La (and C<sub>60</sub>) obtaining ionization energies and electron affinities for the neutral and ionic species within the local-density approximation.<sup>203,204</sup> Saito<sup>205</sup> has also used the local density approximation to calculate the electronic properties of C<sub>80</sub>M (M = K, O, Cl).

Theoretical calculations have been carried out on fullerene-60 derivatives such as hydrofullerenes by Coulombeau and Rassat<sup>184</sup> and by Scuseria<sup>206</sup> who has also considered the perfluorofullerene, C<sub>60</sub>F<sub>60</sub>. Crystal packing considerations for spheroidal molecules including fullerene-60, have been discussed by Williams.<sup>207</sup>

Several papers have focused on the likely electrical and/or magnetic properties of the fullerenes in particular fullerene. 60 Electron Haddon 20239 using HAGO

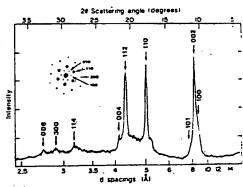


Figure 24. X-ray diffraction pattern of a microcrystalline powder of fullerene-60 obtained by Krätschmer, Lamb. Fostiropoulos. and Huffman. Inset (upper left) is a single-crystal electron diffraction pattern (shown in more detail in Figure 25) indexed with Miller indices compatible with the X-ray pattern. This pattern provided unequivocal evidence that the Co species they had isolated was a round ball 10 Å in diameter in perfect agreement with expectation for buckminsterfullerene (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

and London theory, calculated the ring current magnetic susceptibility and concluded that the shielding should be vanishingly small (less than 1 ppm) due to cancellation of the diamagnetic and paramagnetic contributions. They concluded that fullerene-60 should not show normal aromatic behavior. Studies by Fowler. Lazzeretti, and Zanasi210 and Pauling211 have suggested however that the diamagnetic term has been underestimated. From large scale ab initio, coupled Hartree-Fock calculations (involving all electrons) of the polarizability and magnetizability of C60 and C202+, Fowler et al. 210 conclude that the shielding should be roughly the same as for related aromatic systems. Haddon and Elser<sup>212</sup> have discussed their own results<sup>208,209</sup> and reinterpreted those of Fowler et al.<sup>210</sup> and conclude that the latter study is consistent with a small delocalized susceptibility. Schmalz<sup>213</sup> has argued that the Fowler et al.<sup>210</sup> interpretation is correct. The NMR study of Taylor et al. vielded a chemical shift for fullerene-60 which is fairly typical for an aromatic species. Fowler et al. 214 have extended their approach to the calculation of the shifts in fullerene-70, obtaining results consistent with observation and confirming the line assignments made by Taylor et al.6 This problem is further discussed in section X.

# IX. The Isolation, Separation, and Structural Characterization of Fullerenes-60 and -70

Almost five years, to the day, since the special behavior of the C<sub>60</sub> signal was recognized (Figure 5) and the buckminsterfullerene proposal made,<sup>3</sup> macroscopic samples were isolated and characterized. Krātschmer, Lamb, Fostiropoulos, and Huffman,<sup>4</sup> in following up their earlier IR observations,<sup>5,74</sup> discovered that at ca. 300–400 °C a solid material could be sublimed from the deposit obtained from arc-processed graphite. They found that this sublimate was soluble in benzene and could be crystallized. The X-ray and electron diffraction analyses (Figures 24 and 25) of the crystalline material so obtained (Figure 26) showed it consisted of

Figure 25. Single-crystal electron diffraction pattern of fullerene-60.4 Further details of indices are given in Figure 24 (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).



On Transmitted Light

Figure 26. Transmission micrograph of crystals extracted by Krätschmer et al. from the deposit of arc-processed graphita. Thin platelets, rods and stars of hexagonal symmetry are observed (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

by ca. 3.1 Å (in graphite the interlayer distance is 3.4-3.5 Å). These authors also reported IR (Figure 27), UV/vis, and mass spectra of the extracted material. Bands of  $C_{70}$  were present (weakly) in the IR spectrum and, in the UV/vis spectrum, some features of fullerene-60 were masked by those of fullerene-70. These results provided the first confirmation of the fullerene-60 structural proposal.

In a parallel and independent study of similarly arc-processed carbon, Taylor et al. had also shown that  $C_{60}$  was present by FAB-sampled mass spectrometry and that a red soluble extract could be obtained by treating the carbon deposit directly with benzene. Taylor et al. processed the extract by the Soxhlet procedure and obtained a material which mass spectrometry showed to contain a range of fullerenes,  $C_{60}$  and  $C_{70}$  in particular (Figure 28). This material was and  $C_{70}$  were thereby separated into a magenta and red fractions, respectively. C NMR measurements yielded

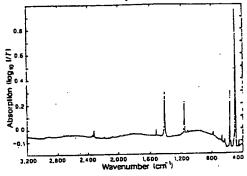


Figure 27. Infrared spectrum of fullerene-60 presented by Krätschmer et al. showing the four fundamentals in excellent agreement with expectation for the proposed fullerene-60 structure. Weaker features belong to fullerene-70 (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

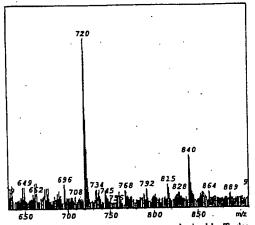


Figure 28. FAB-sampled mass spectrum, obtained by Taylor et al., of the soluble material extracted from arc-processed graphite. Apart from unequivocal evidence for C<sub>60</sub> and C<sub>70</sub> in the extract there is also evidence for other even-numbered carbon species, particularly C<sub>22</sub> and C<sub>32</sub> (reprinted from ref 6; copyright 1990 The Royal Society of Chemistry).

proof that all 60 atoms are equivalent—a result totally commensurate with the buckminsterfullerene structure. There is of course the alternative solution that all the atoms are located on the perimeter of a monocyclic ring. This (explosively) unlikely possibility was eliminated by the NMR spectrum of  $C_{70}$  which consisted of a set of five lines (Figure 29c) with a chemical shift pattern and relative intensities commensurate with the fullerene-70 structure (Figure 30b) first suggested by Heath et al. This result not only confirmed the fullerene 5/6-ring geodesic topology but also eliminated the possibility that the carbon atoms might be fluxional. Almost as important is the confirmation, by this result, of the existence of other members of the fullerene family.

### X. Postbuckminsterfullerene Research—The First Results

Since the revelation that macroscopic samples of the

Trans.

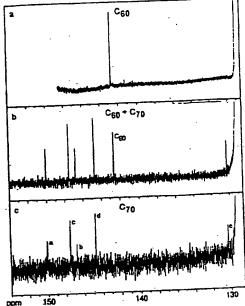


Figure 23. <sup>12</sup>C NMR spectra obtained from chromatographically purified samples (Taylor et al. <sup>9</sup>) of soluble material extracted from are-processed graphite: (a) <sup>12</sup>C NMR spectrum of a purified sample exhibiting only a single resonance, (b) spectrum of a mixed sample, and (c) spectrum of a purified sample of C<sub>10</sub> from which C<sub>20</sub> has been eliminated. These spectra are consistent with the structures and assignments presented in Figure 20. The wing of the intense benzene solvent signal lies to the far right-hand side. This set of observations provided unequivocal evidence that the carbon atoms in C<sub>20</sub> were indeed all equivalent in perfect This set of observations provided unequivocal evidence that the carbon atoms in  $C_{00}$  were indeed all equivalent in perfect agreement with expectation if the molecule were buckminsterfullerene (Figure 30). The five-line spectrum for  $C_{00}$  is also totally consistent with that expected for  $(D_{00})$  fullerene-70 (Figure 30). This spectrum eliminated any lingering doubt there might have been that the C atoms were either fluxional or perhaps located on the perimeter of a monocyclic ring. It also provided evidence for the stability of other members of fullerene family  $^{+6}$  (reprinted from ref 6; copyright 1990 The Royal Society of Chemistry).

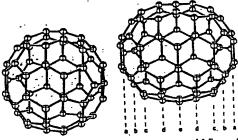


Figure 30. Schematic diagrams of fullerene-60 and fullerene-70 (based on diagrams of Slanina et al. 124). All sixty atoms in fullerene-60 are equivalent whereas fullerene-70 possesses five different types of carbon in the ratios 10:10:20:20:10 in the order schedule respectively as shown. Compare with the NMR spectrum shown in Figure 29.

chromatographically separable, it is now the turn of experimentalist to have a ball. Ajie et al. 12 and Hare trial 22 have observed the UV/visible spectra of chromatographic and the UV/visible spectra of chromatographic spectra of chroma

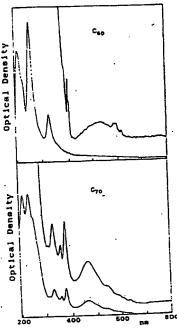


Figure 31. UV/vis spectra of chromatographically separated fullerene-60 and fullerene-70<sup>218</sup> in hexane solution (reprinted from ref 216; copyright 1991 Elsevier Science Publishers).

TABLE I. Properties of C. Buckminsterfullerene

abs(obs)* 528 577 1183	527.1 570.3 1169.1	calc, cm <sup>-1</sup> * 472 618 1119 1434
1429	1406.9	1434

X-ray Data<sup>4</sup>, r(C-C) = 1.388 (9) Å six-six ring fusion r(C-C) = 1.432 (5) Å five-six ring fusion

NMR Date chemical shift (benzene soln) 142.68 ppm

electron affinity ionization energy UV/via banda

Electronic/Spectroscopic Data
2.6-2.8 eV
7.51 (0.02) eV
213, 257, 329 (c<sub>max</sub> = 135,000, 175,000, 51,000)
404 (w) 440-670 (brd) (max. 500, 540, 570, 600, 625) nm

\*Reference 4. \*Reference 218. \*Reference 191. \*Reference 222.

\*See also Figures 24, 32, and 34. /See Figure 28. \*Reference 6 (see also refs 215 and 228). \*Reference 99. \*References 101, 102, 239, and 240. \*Reference 216 (see also ref 215). \*See also Figure 31.

Reber et al. 217 have observed a luminescence spectrum. Frum et al. 218 have observed a most interesting IR emission spectrum from a hot gas-phase fullerene sample. The frequencies of the observed

bands are given in Table I.

The availability of significant quantities of fullerenes has also opened up a Round Postbuckminsterfullerene Era of polycyclic aromatic chemistry. Haufler et al. 29 found that Co can undergo Birch reduction to produce a white solid of formula Co.H.s. They point out that

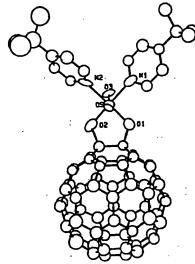


Figure 32. ORTEP drawing (50% ellipsoids) of the one-to-one C<sub>80</sub>-osimium tetroxide adduct C<sub>80</sub>(OsO<sub>4</sub>)(4-tert-butylpyridine); showing the relationship of the osmyl unit with the fullerene-60 carbon network<sup>222</sup> (reprinted from ref 222; copyright 1991 the American Association for the Advancement of Science).

which 12 isolated double bonds remain, possibly in the pentagonal rings. The reduction appears to be reversible. Evidence for the existence of a  $C_{60}U$  complex was obtained by the laser vaporization approach, used originally to detect  $C_{60}La$ . These authors also described the results of cyclic voltammetry measurements which indicated that  $C_{60}$  has two reduction potentials. Similar measurements have been made by Allemand et al. who obtained a third potential. Their cyclic voltammetry measurements indicate that, curiously, fuller-ners-60 and -70 appear to exhibit similar electrochemical behavior.

In one of the first attempts to introduce functional groups, Hawkins et al. 221 have found that they can form adducts of fullerene-60 with OsO4(4-tert-butylpyridine) and its analogues. In a further study Hawkins et al. 222 have now obtained crystals of the osmium complex shown in Figure 32 and shown by X-ray analysis that rotation of the free C50 spheroids in the solid phase has been eliminated by the attached group. This study has yielded the first carbon-carbon bond lengths for the fullerens cage (Table I). Arbogast et al. have observed fascinating photophysical behavior: fullerene-60 shows no fluorescence and efficiently catalyzes the formation of singlet oxygen. These authors observe a amall S-T splitting of ca. 9 kcal/mol which is probably due to the large diameter of the molecule and the resulting small electron electron repulsion energy. This together with the very low fluorescence rate and probably large spin-orbit interaction appears to account for the fact that intersystem crossing is a dominant process. Attention has been drawn to the fact that, due to their photophysical activity, care should be taken when working with fullerenes.

working with runerenes.

Haract al. 224 and Bethune et al. 225 have made infrared measurements on chromatographically separated sam-

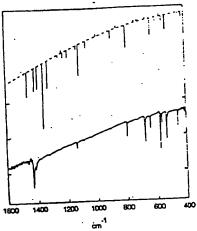


Figure 33. Infrared spectrum of chromatographically purified fullerene-70 obtained by Hare et al. 224 and compared with the calculated spectrum of Bakowies and Thiel. 184.18 The dashed curve is an estimated baseline. Note that the intensity of the very strong band calculated to lie near 1400 cm<sup>-1</sup> has been arbitrarily reduced by a factor of 3 relative to other features. Features calculated to be very weak are indicated by markers above the estimated baseline (reprinted from ref 224; copyright 1991 The Royal Society of Chemistry).

ene-70 together with the calculated spectrum of Bakowies and Thiel 198,199 is presented in Figure 33. Bethune et al. 226 and Dennis et al. 227 have also made Raman measurements of fullerene-60 and -70. Liquidphase NMR studies of unpurified fullerene mixtures by Johnson et al. 228 confirmed the result of Taylor et al.6 (carried out on fully chromatographically purified samples) that the fullerene-60 resonance is a single line. Ajie et al. 215 have also confirmed the NMR measurements of a single line for fullerene-60 and five lines for fullerene-70; the former on a separated sample, the latter on a mixed fullerene 60/-70 sample. A 2D NMR analysis on fullerene-70 by Johnson et al. 229 has unequivocally confirmed the assignments made previously by Taylor et al. shown in Figures 29c and 30b. Further refinements by Fowler et al. 214 of previous studies 210 predict fullerene-60 chemical shifts in excellent agreement with experiment (within 3 ppm). The study also includes estimates of the shifts for fullerene-70 so supporting further the pattern of line assignments given by Taylor et al.<sup>6</sup> (Figures 29c and 30b). Tycko et al.<sup>20</sup> and Yannoni et al.<sup>21</sup> have made solid-state NMR measurements down to 177 K where the motion is sufficiently slow for chemical shift tensor data to be obtained. Fullerene-60 rotates isotropically at 296 K and fullerene 70 rotates somewhat more anisotropically. Haddon et al. 232 have measured the magnetic susceptibility of solid samples of fullerenes and found it consistent with a molecule with a small ring current (see discussion in section VIII). Fowler notes that when this result is compared and contrasted with the NMR shift of fullerene 60° it may imply ambivalent character when the question of the molecules "aromaticity" is considered.

Perhaps scanning tunneling microscopy (STM) offers more than any other a satisfying feeling of what the

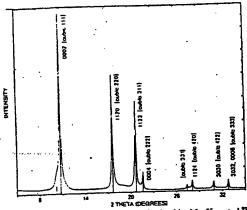


Figure 34. X-rsy diffraction pattern obtained by MacKsy et al. 25 from a chromatographically purified fullerene-60 sample. The structure revealed is basically that of a strongly disordered starking of a simple hexagonal close-packing, exactly as for elemental cobalt. The hexagonal unit cell refines to  $a=10.017\pm0.004$  Å and  $c=16.402\pm0.01$  and contains two  $C_{80}$  spheres. The spheres would be 10.017 Å between centers and the calculated density would be 1.68 g cm<sup>-2</sup>. The lines can be indexed as shown and it will be noted that, because of the stacking disorder, only those reciprocal lattice rows parallel to c for which -h + k = 3n are present. The c/a ratio of 1.637 is very close to the theoretical value of 1.633 and thus the pattern can also be indexed with respect to a face-centered cubic lattice (with a=14.186 Å) (as of copper metal) with stacking disorder which removes the 200 and 400 reflections and which introduces a very weak line (the first) at a spacing of  $a/(8/3)^{1/2}$  due to double diffraction from stacking faults. The intensity variation of the pattern as a whole corresponds to the transform of a sphere of radius 3.5 Å giving a first minimum in the region of  $2\theta=25^\circ$ . Since the crystal is a mixture of FCC and HCP arrays, extracted crystalline material probably contains solvent molecules trapped in the faults.

et al.,<sup>235</sup> and Chen et al.<sup>236</sup> have deposited fullerene monolayers on gold and studied them by STM. The spherical molecules tend to form mobile hexagonally packed arrays on a surface. Chen et al.<sup>236</sup> observed local density variations on the surface of fullerene-60 which are highly suggestive of five- and six-membered rings.

The preliminary X-ray observations were made by Krätschmer et al. working with crystalline material consisting mainly of fullerene-60 with some fullerene-70 present. A recent X-ray diffraction image was obtained by MacKay et al. 231 using chromatographically purified fullerene-60 (Figure 34). This image is commensurate with a completely random mix of HCP and FCC arrays of fullerene-60 molecules. Fleming et al. 228 obtained purely FCC structured crystals from vacuum sublimed material. The implication is that interstitially trapped solvent probably stabilizes the mixed FCC/HCP crystals. It appears that fullerene-60 spheres are rotating in the lattice 231 and that when rotation ceases at low temperature the crystals are still disordered at the atomic level. 221,222,238

A most interesting study as far as theoretical chemistry is concerned is that of Lichtenberger et al.  $^{239,240}$  who measured the photoelectron spectrum of fullerene-60 on a surface and in the gas phase (Figure 35). The results are in good agreement with the theoretical (DV)- $X\alpha$  study of Hale<sup>169</sup> (Figure 23). The first IP of fullerene-60, 7.61 eV, is nicely consistent with the result obtained by Zimmerman et al. 101 and McFlyany. 102

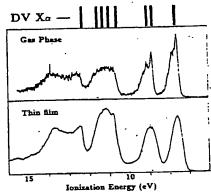


Figure 35. Gas phase (upper) and thin film (lower) He I valence photoelectron spectra of fullerene-60 obtained by Lichtenberger et al.  $^{28340}$  The DV-X $\alpha$  results of Hale  $^{18}$  (see Figure 23) which appear to be in good agreement with observation are indicated (reprinted from ref 239; copyright 1991 Elsevier Science Publishment

Luffer and Schram<sup>241</sup> have made electron ionization mass spectrometric measurements on fullerene-60.

Several papers presented at a special symposium on the fullerenes (Nov 1990) have been collected together and published by Averback et al.<sup>242</sup> Some of the most important experimentally determined properties of fullerenes are presented in the Table I.

### XI. Astrophysical Implications of C60

Although low-temperature ion-molecule processes (Herbst and Klemperer<sup>243</sup> and Dalgarno and Black<sup>244</sup>) can account for most interstellar species, the long cyanopolyynes presented a problem. It was experiments which probed the possibility that carbon stars might be responsible for them<sup>31,32</sup> which revealed the stability of fullerene-60.3 An important aspect of the experiments lay in the possibility of probing the conjecture of Douglas that carbon chains might be responsible for the diffuse interstellar bands (DIBs). The DIBs are a set of interstellar optical absorption features of varying widths which have puzzled astronomers and spectroscopists since the mid-1930s. Herbig has published the definitive analysis of these features. 245,246 Many possible contenders for the carrier have been suggested, however no generally accepted explanation exists so far. This is strange as the species responsible is clearly abundant, chemically bound (i.e. not atomic), and must be quite stable in order to survive in the hostile interstellar environment or, if destroyed, be very efficiently reformed. The types of carrier appear to be few in number and must have very large electronic absorption coefficients.

The possibility that C<sub>50</sub> might be the widely distributed in the Universe and particularly in the outflows from carbon stars was suggested when the original discovery of its stability was made.<sup>2</sup> It was also pointed out that the fullerene-60 surface might be an important site for the catalysis of interstellar reactions and perhaps it (or a derivative) might be responsible for such features as the DIBs. There is one key argument, associated with the proposal that fullerene analogues (ionized or un-ionized complexed or otherwise) may be

the carriers has that all previous suggestions do not fullerene-60 and its analogues are unique in that they appear to survive the violent processes which occur when the atomic components of a chaotic plasma condense to form particles. Various aspects of this original conjecture, particularly with regard to possible derivatives such as intracage complexes both ionized and neutral, have been discussed 55-58 in general terms.

As far as the neutral fullerene-60 species in space is concerned, the negative results of searches based on the laboratory measurement has been published by Snow and Seab<sup>247</sup> and Sommerville and Bellis.<sup>248</sup>

The conditions in the ISM are such that a large fraction of any fullerene-60 molecules present is likely to be ionized and thus it has been pointed out that the spectra of ionized fullerenes such as  $C_{60}^+$  or fullerene analogues (such as the cage complexes  $C_{60}M^+$ ) might be responsible for some astrophysical features. S.5.5 Leger et al. 26 and Joblin et al. 250 have taken up the  $C_{60}^+$  proposal and considered it further.

Complexed species (section VIII) in the interstellar . medium are particularly interesting as any Co present is likely to be ionized and probably have something stuck to its surface. As the DIBs exhibit features reminiscent of matrix spectra, the possibility that intracage complexes 55.57,201-200 as well as the extracage complexes might be responsible has been discussed. Heymann<sup>200</sup> has considered the He intracage complexes and Ballester et al. other likely species containing O, Na, etc. 201 Kroto and Jura 2022 draw particular attention to the fact that the charge transfer bands of the (C<sub>60</sub>M)+ intracage complex and the van der Waals extracage complex (C60)+.M (M = alkali, alkaline earth, or other element) are likely to be very strong. Particularly interesting are possible relationships that charge-transfer transitions might have with the DIBs and perhaps also the strong unassigned 2170 Å absorption feature which has puzzled astronomers for over seven decades. Hoyle and Wickramasinghe251 suggested that C50 itself might explain this feature and further calculations relating to this possibility have been discussed by Braga et al. 167 Rabilizirov 252 has also discussed these possibilities. Wright 253 has discussed the general optical/UV characteristics of fullerenes and concludes that the observed interstellar extinction is not consistent with the presence of significant quantities of spheroidal particles with graphite-like outer shells. In this respect the existence of the amorphous carbon surface layers surrounding the graphite cores of carbon microparticles may well be important.116 From the UV/vis spectra obtained so far 4215.216 it is clear that neutral fullerene-60 is not responsible for either the DIBs or the 2170 Å hump.

There are also some intriguing interstellar emission features in the IR, termed the unidentified infrared bands (UIBs), which have been assigned to PAH-like material by Duley and Williams, 254 Lêger and Puget, 253 and Allamandola et al. 256 The assignment rests largely on the reasonable correspondence between the astrophysical frequencies and those of polycyclic aromatic molecules which are usually used for fingerprint identification of large PAHs. Balm and Kroto 257 have discussed the fact that, if the fullerene-60 concept is correct, PAH material in space is likely to be nonplanar. They point out that one feature, namely that at 11.3

The new results also offer possible new avenues of study as far as condensed carbonaceous matter in the cosmos is concerned. According to McKay et al.258 caged carbon clusters may offer a plausible explanation of some of the isotope anomalies observed in the elemental analysis of carbonaceous chondrites particularly the 22Ne anomaly. Clayton 259 has pointed out that condensation in the atmospheres of supernovae might explain the so-called Ne–E anomaly. McKay et al. 258 have suggested that this observation might be explained by encapsulation of "Na in fullerene cages or icospiral embryos during the dust formation phases that follow supernova and nova outbursts. Subsequently, the decay <sup>22</sup>Na yields an encapsulated <sup>22</sup>Ne atom. Zinner et al.250 have pointed out that isotope anomalies are only to be found in spheroidal carbon grains. So far the only evidence that C<sub>60</sub> might exist in space is an unconfirmed report by Anderson. 261

### XII. Conclusions

It took some 15 of so years before the imaginative theoretical conjectures of Osawa and Yoshida<sup>13,14</sup> and Bochvar and Gal pern<sup>17,18</sup> were realized in the discovery of the stability of the C<sub>50</sub> mass spectrometric signal<sup>3</sup> in 1985: A further period of five years elapsed during which time many experimental measurements and theoretical studies were made. By-and-large the theoretical work (section VIII) substantiated the idea that buckminsterfullerene should be stable. As time elapsed the weight of circumstantial evidence grew and ultimately became convincing. The key observations include:

(1) Detection of monometallic complexes indicated that atom encapsulation was feasible.<sup>7,96</sup>

(2) Further cluster beam studies showed 60 to be a magic number whether the carbon species was positively or negatively charged or neutral. 64.56.52

(3) Reactivity studies showed the molecule to possess an inertness that was consistent with closure and the

absence of dangling bonds. 103,96

(4) The pentagon isolation principle explained the observation of  $C_{60}$  as the first magic number and  $C_{70}$  as the second. Thus it was shown that the fullerene hypothesis rested on the observation of two magic numbers and not just one. Further refinement of the geodesic principle explained other observed magic numbers.  $^{1.9}$ 

(5) Large fullerene networks were found to possess quasiicosahedral structures and thus related giant concentric cage species<sup>108</sup> appeared to explain the infrastructure of the carbon microparticles observed by lijima.<sup>109,110</sup>

(6) Photoelectron measurements of Yang et al. 99 were also quite consistent with the fullerene conjecture.

These and other studies (discussed in sections V-VII) thus had laid the background against which the critical infrared observation of Krätschmer et al. 5.74 was made. They were led to make this observation by considering that some intriguing optical features observed in 1982 might be due to buckminsterfullerene. These observations were followed up by Krätschmer, Lamb, Fostiropoulos, and Huffman and Taylor et al., and the results have revolutionized the field in that now the material can be made in quantity and the properties of

It is interesting to note that the motives for the experiments which serendipitously revealed the spontaneous creation and remarkable stability of C60 were astrophysical. Behind this goal lay a quest for an understanding of the curiously pivotal role that carbon plays in the origin of stars, planets, and biospheres. Behind the recent breakthrough of Krätschmer et al. in producing macroscopic amounts of fullerene-60, lay similar astrophysical ideas.4 It is fascinating to now ponder over whether buckminsterfullerene is distributed throughout space, and we have not recognized it. and that it may have been under our noses on earth, or at least played an important role in some very common environmental processes, since time immemorial.

The material is already exhibiting novel physical and chemical properties and there can be little doubt that an exciting field of chemistry and materials science, with many exciting applications has opened up. One of its most important properties is its ability to accept electrons. The low-lying LUMO causes it to be a soft electrophile.

It is perhaps worthwhile noting that C60 might have been detected in a sooting flame decades ago and that our present enlightenment has been long delayed. How serious this delay has been only time will tell; however, already fullerene chemistry is a vibrant field of study and the prospects for new materials with novel properties is most promising. Certainly, a New Round Postbuckminsterfullerene World of carbon chemistry appears to have been discovered, almost overnight. It should not be long before the molecule becomes a standard in textbooks; indeed construction procedures for fullerene-60 and giant fullerenes are to be found in the educational literature. 126,262

### Warning

The UCLA group has pointed out the importance of treating the material with great caution at this time when so little is known about it.<sup>263</sup> Its ability to catalyze the formation of singlet oxygen and its novel chemical behavior inevitably suggest the possibility that the fullerenes might be carcinogenic. Particular care should be taken to ensure that the dust is not inhaled during preparation of the soot itself.

Acknowledgments. We are very happy to acknowledge the help of David Walton and Roger Taylor for helping to eliminate several obscurities from this article. We also thank Patrick Fowler for his help. Thanks are also due to all those who kindly sent reprints and we are grateful for permission to publish the data from several groups. S.P.B. thanks the SERC and AWA the Syrian Atomic Energy Commission for financial support.

### References

AN AND THE STREET

- Palmer, H.; Shelef, M. Chemistry and Physics of Carbon; Walker, J. R., Jr., Ed.; Marcel Dekker: New York, 1967; Vol. 4, pp 85–135.
   Weltner, W., Jr.; Van Zee, R. J. Chem. Rev. 1989, 89, 1713–1747.
   Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smelley, R. E. Nature (London) 1985, 318, 162–163.
   Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. Nature (London) 1990, 347, 354–358.
   Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. Dusty Objects in the Universe; Bussoletti, E., Vittone, A. A., Eds.;

- Krote et a.

  Kluwer: Dordrecht, 1990 (Conference in 1989).

  (6) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. J. Chem. Soc., Chem. Commun. 1990, 1223-1425.

  (7) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F. Kroto, H. W.; Smalley, R. E. J. Am. Chem. Soc. 1985, 167, 7779-7780.

  (8) Kroto, H. W. Nature (London) 1987, 329, 529-531

  (9) Schmalz, T. G.; Seitz, W. A.; Klein, D. J.; Hite, G. E. J. Am. Chem. Soc. 1988, 110, 1113-1127.

  (10) Kroto, H. W.; Walton, D. R. M. Chemistry of Three Dimensional Polycyclic Molecules: Osawa, E. Yonemitsu, O. Eds. Verlag Chemie International: Weinheim, in press. Verlag Chemie International: Weinheim, in press. (12) Reti, L., Ed. The Unknown Leonardo; McGraw Hill Newport, 1974; pp 71.

  (11) Osawa, E. Kagaku (Kyoto) 1970, 25, 854-863 (in Japanese). Chem. Abstr. 1971, 74, 75698v.

  (12) Yosahida, Z.; Osawa, E. Aromaticity; Kagakudojin: Kyoto. 1971; pp 174-178 (in Japanese). (13) Jones, D. E. H. New Sci. 32 (3) Nov) 1966, 245.

  (15) Jones, D. E. H. New Sci. 32 (3) Nov) 1966, 245.

  (16) Jones, D. E. H. New Sci. 32 (3) Nov) 1966, 245.

  (17) Bochver, D. A.; Gal'pern, E. G. Dokl. Akad. Nauk SSSR 1973, 209, 610-612; Proc. Acad. Sci. USSR 1973, 209, 239-241 (English translation).

  (18) Stankevich, I. V.; Nikerov, M. V.; Bochvar, D. A. Russ. Chem.

- (English translation).
  Stankevich, L. V., Nikerov, M. V., Bochvar, D. A. Russ. Chem.
- Stankevich, I. V., Nikerov, M. V., Bochvar, D. A. Russ. Chem. Rev. 1984, 53(7), 640-655.
  Davidson, R. A. Theor. Chim. Acta 1981, 58, 193-195.
  Haymet, A. D. J. Chem. Phys. Lett. 1985, 122, 421-424
  Dörnenburg, E.; Hintenberger, H. Z. Naturforsch. Teil A 1959, 14A, 765-767.
  Dörnenburg, E.; Hintenberger, H.; Franzen, J. Z. Naturforsch. Teil A 1961, 16A, 532-534.
  Franzen, J.; Hintenberger, H. Z. Naturforsch. Teil A 1961, 16A, 535-539.
- (22)

- 16A, 535-539.
   164 Hintenberger, H.: Franzen, J.: Schuy, K. D. Z. Naturjorsch Teil A 1965, 18A, 1236-1237.
   125 Rohlfing, E. A.: Cox, D. M.: Kaldor, A. J. Chem. Phys. 1984, 81, 332-3330.
   126 Dietz, T. G.: Duncan, M. A.; Powers, D. E.: Smalley, R. E. J. Chem. Phys. 1981, 74, 5511-6512.
   127 Kaldor, A.; Cox, D. M.: Trevor, D. J.; Whetten, R. L. Catalist Characterisation Science; Deviney, M. L.; Gland, J. L., Eds.; American Chemical Society: Washington, DC. 1985: pp 111-123. 111-123

- Bloomfield, L. A.; Geusic, M. E.; Freeman, R. R.; Brown, W. L. Chem. Phys. Lett. 1985, 121, 33-37.
   Heath, J. R.; Zhang, Q.; O'Brien, S. C.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. J. Am. Chem. Soc. 1987, 109, 359-363.
   Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. Astrophys. J. 1987, 314, 352-355.
   Kroto, H. W. Chem. Soc. Rev. 1982, 11, 435-491.
   Kroto, H. W. Int. Rev. Phys. Chem. 1981, 1, 309-376.
   Alexander, A. J.; Kroto, H. W.; Walton, D. R. M. J. Mol. Spec. 1976, 62, 175-180.
   Kroty, C.; Kroto, H. W.; Walton, D. R. M. J. Mol. Spec. 1980. 261-265.

- 261-265.

- 261-265.
  Oka, T. J. Mol. Spec. 1978, 72, 172-174.
  Avery, L. W.; Broten, N. W.; Macleod, J. M.; Oka, T.; Kroto, H. W. Astrophys. J. 1976, 205, L173-L175.
  Kroto, H. W.; Kirby, C.; Walton, D. R. M.; Avery, L. W.; Broten; N. W.; Macleod, J. M.; Oka, T. Astrophys. J. 1978, 219, L133-L137.

- Broten; N. W.; Mackood, J. M.; Oka, T. Astrophys. J. 1978, 219, L133-L137.

  (38) Broten, N. W.; Oka, T.; Avery, L. W.; Mackod, J. M.; Kroto, H. W. Astrophys. J. 1978, 223, L105-L107.

  (39) Bell, M. B.; Feldman, P. A.; Kwok, S.; Matthews, H. E. Nature (London) 1982, 295, 389-391.

  (40) Douglas, A. E. Nature (London) 1977, 269, 130-132.

  (41) Michalopoulos, D. L.; Geusic, M. E.; Langridge-Smith, P. R. R.; Smalley, R. E. J. Chem. Phys. 1984, 80, 3556-3560.

  (42) Kroto, H. W. Proc. R. Inst. 1986, 58, 45-72.

  (43) Fuller, R. B. Inventions—The Futented Works of Buckminster Fuller; St. Martin's Press: New York, 1983.

  (44) Nickon, A.; Silversmith, E. F. Organic Chemistry—The Name Game: Modern Coined Terms and Their Origins; Pergamon: New York, 1987; pp 214-215.

  (45) Kroto, H. W. Nature (London) 1986, 319, 444.

  (46) Kroto, H. W. Nature (London) 1986, 322, 766.

  (47) Rose, P. Private communication (Figure 7).

  (48) Castells, J.; Serratosa, F. J. Chem. Ed. 1983, 60, 941.

  (49) Castells, J.; Serratosa, F. J. Chem. Ed. 1983, 63, 630.

  (50) Kroto, H. W. Science 1988, 242, 1139-1145.

  (51) Carl, R. F.; Smalley, R. E. Science 1988, 242, 1017-1022.

  (52) Hesth, J. R.; O'Brien, S. C.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. Comments Condens. Matter Phys. 1987, 13, 119-141.

- 119-141. Smalley, R. E. Carbon in the Galaxy, Tarter, J. C., Chang, S., DeFreta, D. J., Eda.; National Aeronautics and Space Administration Conference Publication 3061: Washington, DC. 1990; no 199-242.

(54) Smalley, R. E. Atomic and Molecular Clusters: Bernstein, E. R., Ed.: Elsevier. Amsterdam. 1990; pp 1-68.
(55) Krota, H. W. Polycyclic Aromatic Hydrocarbons and Astrophysics: Leger, A., d'Hendecourt, L. B., Eda.; Reidel: Dordrecht, 1987; pp 197-206.
(56) Krota, H. W. Phil. Trans. R. Soc. Lond. A 1988, 325, 405-421.
(57) Krota, H. W. Ann. Phys. Fr. 1989, 14, 169-179.
(58) Krota, H. W. Carbon in the Galaxy, Tarter, J. C., Chang, S., DeFrees, D. J., Eds.; National Aeronautics and Space Administration Conference Publication 3061: Washington, DC, 1990; pp 275-284.

(59)

ministration Conference Publication 3061: Washington, D., 1990; pp 27:5-284.

Kroto, H. W. Math. Applic. 1989, 17, 417-423.

Kroto, H. W. Chem. Brit. 1990, 26, 40-45.

Kroto, H. W. Pure Appl. Chem. 1990, 62, 407-415.

Kroto, H. W. Pure Appl. Chem. 1990, 62, 407-415.

Kroto, H. W. Pure Appl. Chem. 1990, 62, 407-415.

Kroto, H. W. Pure Appl. Chem. 1990, 536-43.

Heath. J. R. Spectroscopy 1990, 5, 36-43.

Heath. J. R. Spectroscopy 1990, 5, 36-43.

Heath. J. R. Spectroscopy 1990, 5, 36-43.

Heath. J. R. F.: Kroto, H. W.: Smalley, R. E. Chem. Phys. Lett. 1986, 126, 215-217.

Hahn, M. Y.: Honea, E. C.: Paguia, A. J.: Schriver, K. E.: Camarerna, A. M.: Whetten, R. L. Chem. Phys. Lett. 1986, 130, 12-16.

(65)

Camarena, A. M.; Whetten, R. L. Chem. Phys. Lett. 130, 12-16.

(66) O'Brien, S. C.; Heath, J. R.; Kroto, H. W.; Curl, R. F.; Smalley, R. E. Chem. Phys. Lett. 1986, 132, 99-102.

(67) Cox, D. M.; Reichmann, K. C.; Kaldor, A. J. Chem. Phys. 1988, 88, 1588-1597.

(68) O'Keefe, A.; Rosa, M. M.; Baronavski, A. P. Chem. Phys. Lett. 1986, 130, 17-19.

(69) Pradel, P.; Monchicourt, P.; Laucagne, J. J.; Perdrix, M.; Watel, G. Chem. Phys. Lett. 1989, 158, 412-416.

(70) McElvany, S. W.; Nelson, H. H.; Baronavski, A. P.; Watson, C. H.; Eyler, J. R. Chem. Phys. Lett. 1987, 134, 214-219.

(71) McElvany, S. W.; Dunlap, B. L.; O'Keefe, J. J. Chem. Phys. 1987, 86, 715-725.

(72) Meijer, G.; Bethune, D. S. Chem. Phys. Lett. 1990, 178, 1930

1987, 86, 715-725.
Meijer, G.; Bethune, D. S. Chem. Phys. Lett. 1990, 175, 1-2.
Meijer, G.; Bethune, D. S. J. Chem. Phys. 1990, 93, 7800-7802.

(75)

(73) Meijer, G.; Bethune, D. S. J. Chem. Phys. 1990, 93, 17800-7802.
(74) Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. Chem. Phys. Lett. 1990, 170, 157-170.
(75) Creasy, W. R.; Brenna, J. T. J. Chem. Phys. 1990, 92, 2259-2279.
(76) Creasy, W. R.; Brenna, J. T. Chem. Phys. 1988, 126, 453-468.
(77) Campbell, E. E. B.; Ulmer, G.; Hasselberger, B.; Busmann, H.-G.; Campbell, E. E. B.; Ulmer, G.; Hasselberger, B.; Busmann, H.-G.; Campbell, E. E. B.; Busmann, H.-G.; Campbell, E. E. B.; Ulmer, G.; Busmann, H.-G.; Campbell, E. E. B.; Ulmer, G.; Busmann, H.-G.; Hertel, I. V. Chem. Phys. Lett. 1990, 175, 505-510.
(79) Campbell, E. E. B.; Ulmer, G.; Busmann, H.-G.; Hertel, I. V. Chem. Phys. Lett. 1990, 175, 505-510.
(80) Greenwood, P. F.; Strachan, M. G.; El-Nakat, H. J.; Willer, G. D.; Wilson, M. A.; Attalla, M. I. Fuel 1990, 69, 257-260.
(81) Giardini Guidoni A.; Teptil, R.; Morone, A.; Spela, M.; Mele, A.; Letardi, T.; Di Lezzaro, P. Proceedings of Laser 89 Conference, manuscript 0913, in press.
(82) Lineman, D. N.; Somayajula, K. V.; Sharkey, A. G.; Hercules, D. M. J. Phys. Chem. 1983, 23, 5025-5026.
(83) Lineman, D. N.; Viswanadham, S. K.; Sharkey, A. G.; Hercules, D. M. Microbeam Anal. 1889, 24, 297-298.
(84) So, H. Y.; Wilkins, C. L. J. Phys. Chem. 1983, 93, 1184-1187.
(85) Rubin, Y.; Kahr, M.; Knobler, C. B.; Whetten, R. L.; Schriver, K. E.; Houk, K. N.; Li, Y. Science 1983, 245, 1038-1090.
(87) Gerbardt, Ph.; Löffler, S.; Homann, K. Chem. Phys. Lett.

· 一种多种的

1 1: .

and some

¥.

(88)

Schriver, K. E.; Houk, K. N.; LI, Y. Schene 1363, 265, 1088-1090.
Gerhardt, Ph.; Löffler, S.; Homann, K. Chem. Phys. Lett. 1987, 137, 306-310.
Gerhardt, Ph.; Homann, K. H.; Löffler, S.; Wolf, H. AGARD Conf. Proc. 1987, 422, 22-(1-11).
Gerhardt, Ph., Löffler, S.; Homann, K. H. Symposium on Combustion 1988, 22, 395-401.
Gerhardt, Ph.; Homann, K. H. J. Phys. Chem. 1990, 94, 2201, 1820. (90)

Gerhardt, Ph.; Homann, K. H. J. Phys. Chem. 1990, 94, 5381-5391.
 Cox. D. M.; Trevor, D. J.; Reichmann, K. C.; Kaldor, A. J. Am. Chem. Soc. 1986, 108, 2457-2458.
 Radi, P. P.; Bunn, T. L.; Kemper, P. R.; Molchan, M. E.; Bowers, M. T. J. Chem. Phys. 1988, 88, 2809-2814.
 Radi, P. P.; Hsu, M. T.; Brodbelt-Lustig, J.; Rincon, M. E.; Bowers, M. T. J. Chem. Phys. 1990, 92, 4817-4822.
 Radi, P. P.; Hsu, M. T.; Rincon, M. E.; Kemper, P. R.; Bowers, M. T. Chem. Phys. Lett. 1990, 174, 223-229.
 O'Brien, S. C.; Heath, J. R.; Curl, R. F.; Smalley, R. E. J. Chem. Phys. 1988, 88, 220-230.
 Weiss, F. D.; Elkind, J. L.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. J. Am. Chem. Soc. 1988, 110, 4464-4465.
 Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. Unpublished observations.
 Heath, J. R.; Curl, R. F.; Smalley, R. E. J. Chem. Phys. 1987, 4236-4238.

87, 4236-4238.

(100) Cheshnovsky, O.; Yang, S. H.; Pettiette, C. L.; Craycraft, M. J.; Liu, Y.; Smalley, R. E. Chem. Phys. Lett. 1987, 138, 119-124.

(101) Zimmerman, J. A.; Eyler, J. R.; Bach, S. B. H.; McElvany, S. W. J. Chem. Phys. 1991, 94, 3556-3562.
(102) McElvany, S. W. Int. J. Mass Spectrom. Ion Process 1990, 102, 81-98.

Zhang, Q. L.; O'Brien, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Zhang, Q. L.; O'Brien, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Zhang, Q. L.; O'Brien, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Zhang, Q. L.; O'Brien, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Zhang, Q. L.; O'Brien, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Zhang, Q. L.; O'Brien, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Zhang, Q. L.; O'Brien, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Zhang, Q. L.; O'Brien, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Zhang, Q. L.; O'Brien, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Zhang, Q. L.; O'Brien, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Zhang, Q. L.; Curl, R. L.; Zhang, Q. Kroto, 17 525–528.

525-528.
Rohlfing, E. A. J. Chem. Phys. 1990, 93, 7851-7862.
Hallett, R. A.; McKay, K. G.; Balm, S. P.; Allaf, A. W.; Kroto, H. W.; Stace, A. J. In press.
Doverstal, M.; Lindgren, B.; Sassenberg, U.; Yu, H. Phys.

(106) Doverstel, M.; Lindgren, B.; Sassenberg, U.; 1u, R. Phys. Scripta 1991, in press.
 (107) Fowler, P. W.; Steer, J. I. J. Chem. Soc., Chem. Commun. 1987, 1403-1405.
 (108) Kroto, H. W.; McKay, K. G. Nature (London) 1988, 331;

328-331. Ijima, S. J. Cryst. Growth 1980, 5, 675-683. Ijima, S. J. Phys. Chem. 1987, 91, 3466-3467. Ilima, S. G., Wales, D. J., Kroto, H. W. To be published. Kroto, H. W. J. Chem. Soc., Faraday Trans. 1990, 86, 9455-

(112) Kroto, H. W. J. Chem. Soc., Faraday Praks. 1936, 68. 2465-2468.
(113) Roulston, S. A.; Dunne, L. J.; Clark, A. D.; Chaplin, M. F. Philo. Mag. B. 1990, 62, 243-260.
(114) Yacaman, M. J.; Cox, D.; Chianelli, R.; Kaldor, A. Icosahedral Spirals in Giant Fullerene Solids. In preparation. of Spirals in Giant Fullerene Solids. In preparation. (115) Yacaman, M. J. Proceedings of Symposium G on Clusters and Cluster-Assembled Materials. Mater. Res. Soc. Proc. Averback, R.-S., Nelson, D. L., Bernholt, J., Eds.; MRS Publications: New York, 1991.
(116) Kroto, H. W.; Ijima, S. In press.
(117) Wales, D. J. Chem. Phys. Lett. 1987, 141, 478-484.
(118) Bernholt, J.; Phillips, J. C. J. Chem. Phys. 1986, 85, 3258-3267.
(119) Kroto, H. W. 19th Biennial Conference on Carbon; American and Conference on Carbon; American and Canternal Conference on Carbon; American Canternal C

(119) Kroto, H. W. 19th Biennial Conference on Carbon; American Carbon Society, 1989; pp 394-395.
 (120) Frenklach, M.; Ebert, L. B. J. Phys. Chem. 1988, 92, 561-563.
 (121) Ebert, L. B.; Scanlon, J. C.; Clausen, C. A. Energy Fuels 1988, 92, 262-465.

31-52 (125) Kroto, H. W. To be published. (126) Kroto, H. W.; McKay, K. G. J. Chem. Ed. To be submitted. (127) Stone, A. J.; Wales, D. J. Chem. Phys. Lett. 1986, 128, (127) 501-503.

 Sol-503.
 Takai, T.; Lee, C.; Halicioglu, T.; Tiller, W. A. J. Phys. Chem. 1990, 94, 4480-4482.
 Balm, S. P.; Allaf, A. W.; Kroto, H. W.; Murrell, J. N. J. Chem. Soc., Faruday Trans. 1991, 87, 803-806.
 Zerbetto, F. Chem. Phys. Lett. 1991, 150, 39-45.
 Blone, P.; Milani, P. Phys. Rev. B 1990, 42, 3201-3204.
 Schmalz, T. G.; Seitz, W. A.; Klein, D. J.; Hite, G. E. Chem. Phys. Lett. 1986, 130, 230-207.
 Hosoya, H. Comp. Maths., Appl. 1986, 12, 271-275.
 Brendsdal, E.; Cyvin, S. J. THEOCHEM 1989, 57, 55-66.
 Elser, V. Counting the Kekule Structures of Buckminsterfullerene. Personal communication. fullerene. Personal communication.

Klein, D. J.; Schmalz, T. G.; Hite, G. E.; Seitz, W. A. J. Am.

(136) Klein, D. J.; Schmair, T. G.; Hile, G. E.; Seikl, W. A. S. All. Chem. Soc. 1985, 108, 1301-1302.
(137) Klein, D. J.; Seitz, W. A.; Schmalt, T. G. Nature (London) 1986, 323, 703-706.
(138) Randie, M.; Nicolie, S.; Trinajstic, N. Croat. Chem. Acta. 1207 of 150. 2014

(138) Nicolie, S.; Trinaistic, N. Kem. Ind. (Zagreb) 1987, 36, 107-111.

(140) Amic, D., Trinajstic, N. J. Chem. Soc., Perkin Trans. 2 1990, 1595-1598.

Belesubramanian, K.; Liu, X. J. Comput. Chem. 1988, 9,

406-415.
(142) Balasubramanian, K. Chem. Phys. Lett. 1990, 175, 273-278.
(143) Dias, J. R. J. Chem. Educ. 1983, 66, 1012-1015.
(144) Haymet, A. D. J. J. Am. Chem. Soc. 1986, 108, 319-321.
(145) Jiang, Y.; Zhang, H. Theor. Chem. Acta 1989, 75, 279-297.
(146) Hess, R. A. Schand, L. J. J. Org. Chem. 1986, 51, 3902-3903.
(147) Albara, J.; Hosoya, H. Bull. Chem. Soc. Jpn. 1988, 61, 2557-2659.

(148) Fowler, P. W.; Woolrich, J. Chem. Phys. Lett. 1986, 127, 78-83.

18-83.
(149) Fowler, P. W. Chem. Phys. Lett. 1385, 131, 444-450.
(150) Fowler, P. W.; Cremona, J. E.; Steer, J. L. Theor. Chim. Acta. 1388, 73, 1-26.
(151) Fowler, P. W. J. Chem. Soc., Faraday Trans. 1990, 86,

- (152) Ceulemana, A.; Fowler, P. W. Phys. Rev. A. 1989, 29, 481-493.
   (153) Ceulemana, A.; Fowler, P. W. J. Chem. Phys. 1990, 93, 1221-1234.
- 1221-1234.
  (154) Byers Brown, W. Chem. Phys. Lett. 1987, 136, 128-133.
  (155) Coulombeau, C.; Rassat, A. J. J. Chim. Phys. Phys.-Chim. Biol. 1987, 84, 875-882.
  (156) Ozaki, M.; Takahashi, A. Chem. Phys. Lett. 1986, 127, 2006.

- (156) Ozzki, M.; Takahashi, A. Chem. Phys. Lett. 1886, 127. 242-244.
  (157) Haddon, R. C.; Brus, L. E.; Raghavachari, K. Chem. Phys. Lett. 1886, 125, 459-464.
  (158) Haddon, R. C.; Brus, L. E.; Raghavachari, K. Chem. Phys. Lett. 1886, 131, 165-169.
  (159) Bochar, D. A.; Gal'pern, E. G.; Stankevich, I. V. Zh. Strukt. Khim. 1889, 30, 38-43 (in Russian).
  (160) Feng, J.; Li, J.; Wang, Z.; Zerner, M. C. Int. J. Quantum Chem. 1990, 37, 599-607.
  (161) Newton, M. D.; Stanton, R. E. J. Am. Chem. Soc. 1986, 108, 108.
- (161) Newton, M. D.; Stanton, R. E. J. Am. Chem. Soc. 1986, 108, 2469-2470.
- (162) McKee, M. L.; Herndon, W. C. J. Mol. Struct. 1987, 153.
- (162) McKee, M. L.; Herndon, W. C. J. Mol. Struct. 1981, 1931, 75-84.
  (163) Lüthi, H. P.; Almlöf, J. Chem. Phys. Lett. 1987, 135, 357-360.
  (164) Almlöf, J.; Lüthi, H. P. ACS Symp. Ser. 1987, 353 (Supercomput. Res. Chem. Chem. Eng.], 35-48.
  (165) Almlöf, J. Carbon in the Galaxy: Tarter, J. C. Chang, S. DeFrees, D. J., Eds.; National Aeronautics and Space Administration Conference Publication 3061: Washington, DC, 1990; pp 245-258.
  (166) Larsson, S.; Volosov, A.; Rosen, A. Chem. Phys. Lett. 1987, 137, 501-504.
  (167) Braga, M.; Larsson, S.; Rosen, A.; Volosov, A. Astron. Astrophys. 1991, 245, 232-238.
  (168) Schulman, J. M.; Disch, R. L. J. Chem. Soc., Chem. Comm. 1991, 411-412.

- 1991, 411-412.

  (169) Hale, P. D. J. Am. Chem. Soc. 1986, 108, 6087-6088.

  (170) Satpathy, S. Chem. Phys. Lett. 1986, 130, 545-550.

  (171) Marynick, D. S.; Estreicher, S. Chem. Phys. Lett. 1986, 132, 383-386.
- 383-386.
  (172) Kovacevič, K.; Graovac, A.; Babič, D. Int. J. Quantum Chem. Symp. 1987, 21, 589-593.
  (173) Haddon, R. C. J. Am. Chem. Soc. 1990, 112, 3385-3389.
  (174) Fabre, C.; Rassat, A. C.R. Acad. Sci. Paris 1990, t. 308 II., 1223-1228.
- Kataoka, M.; Nakajima, T. Tetrahedran 1986, 42, 6437-6442.
   Lāzlô, I.; Udvardi, L. Chem. Phys. Lett. 1987, 136, 418-422.
   Shibuya, T.-L.; Yoshitani, M. Chem. Phys. Lett. 1987, 137,
- (177)Hayden, G. W.; Mele, E. J. Phys. Rev. B 1987, 36, 5010-5015. Negri, F.; Orlandi, G.; Zerbetto, F. Chem. Phys. Lett. 1988. 13-16
- 144, 31-37. Wu, Z. C.; Jelski, D. A.; George, T. F. Chem. Phys. Lett. 1987, 137, 291-294.
- Disch, R. L.; Schulman, J. M. Chem. Phys. Lett. 1986, 125, (181)
- 465-466.
  (182) Schulman, J. M.; Disch, R. L.; Miller, M. A.; Peck, R. C. Chem, Phys. Lett. 1987, 141, 45-47.
  (183) Coulombeau, C.; Rassat, A. J. J. Chim. Phys. Phys.-Chim. Biol. 1987, 84, 875-882.
  (184) Coulombeau, C.; Rassat, A. J. J. Chim. Phys. Phys.-Chim. Biol. 1988, 85, 369-374.
  (185) Weeks, D. E.; Harter, W. G. Chem. Phys. Lett. 1986, 132, 387-392.
- Weeks, D. E.; Harter, W. G. Chem. Phys. Lett. 1988, 144, 366-372.
- (187) Weeks, D. E.; Harter, W. G. J. Chem. Phys. 1989, 90, 4727-4743.
- Weeks, D. E.; Harter, W. G. J. Chem. Phys. 1989, 90, 4744-4771. (188)
- (189) Weeks, D. E.; Harter, W. G. Chem. Phys. Lett. 1991, 176,
- Stanton, R. E.; Newton, M. D. J. Phys. Chem. 1988, 92, (190) 2141-2145

- 2141-2145.
  (191) Cyvin, S. J.; Brendsdal, E.; Cyvin, B. N.; Brunvoll, J. Chem. Phys. Lett. 1988, 143, 377-380.
  (192) Brendsdal, E.; Cyvin, B. N.; Brunvoll, J.; Cyvin, S. J. Spectrosc. Lett. 1988, 21, 313-318.
  (193) Brendsdal, E.; Spectrosc. Lett. 1988, 21, 319-339.
  (194) Slanina, Z.; Rudzinski, J. M.; Togasi, M.; Osawa, E. THEO-CHEM 1989, 61, 169-176.
  (195) Slanina, Z.; Rudzinski, J. M.; Osawa, E. Collect. Czech. Chem. Commun. 1987, 52, 2831-2838.
  (196) Slanina, Z.; Rudzinski, J. M.; Osawa, E. Carbon 1987, 25, 747-750.

STATE OF THE STATE OF THE RESERVE OF THE PARTY OF THE

- (197) Rudzinski, J. M.; Slanina, Z.; Tograi, M.; Osawa, E.; lizuka, T. Thermochim. Acta 1988, 125, 155-162.
  (198) Bakowies, D.; Thiel, W. J. Am. Chem. Soc. 1991, 113, 3704-3714.
- 3/04-3/14.
   Bakowies, D.; Thiel, W. Chem. Phys. 1991, 151, 309-321.
   Heymann, D. J. Geophys. Res., B 1986, 91, E135-138.
   Ballester, J. L.; Antoniewicz, P. R.; Smoluchowski, R. Astro-

- (202) Kroto, H. W., Jura, M. In press. (203) Rosen, A.; Waestberg, B. J. Am. Chem. Soc. 1988, 110, 8701-8703.
- (204) Rosen, A.; Waestberg, B. Z. Phys. D: At. Mol. Clusters 1989, 12, 387-390.
- 12. 387-390.

  (205) Saito, S. Proceedines of Symposium G on Clusters and Cluster-Assembled Materials, Mater. Res. Soc. Proc., Averback, R. S., Nelson, D. L., Bernhole, J., Eda.; MRS Publications: New York, 1991.

  (206) Scuseria, G. E. Chem Phys. Lett. 1991. 176, 423-427.

  (207) Williams, D. E. G. J. Chem. Phys., 1987, 87, 4207-4218.

  (208) Elser, V.; Haddon, R. C., Natire (London) 1987, 325, 792-794.

  (209) Elser, V.; Haddon, R. C., Phys. Rev. A 1987, 36, 4579-4584.

  (210) Fowler, P. W., Lazzeretti, P., Zanasi, R. Chem. Phys. Lett. 1990, 165, 9-25.

  (211) Pauling, L., Unpublished work.

  (212) Haddon, R. C.; Elser, V. Chem. Phys. Lett. 1990, 169, 362-364.

- 1822 Haddon, R. C.; Elser, V. C. L. L. W. L. L. H. 1990, 175, 3-5.
   182-364.
   183 Schmalz, T. G. Chem. Phys. Lett. 1990, 175, 3-5.
   184 Fowler, P. W.; Lazzeretti, P.; Malsgoli, M.; Zanasi, R. Chem. Phys. Lett. 1991, 179, 174-180.
   185 Ajie, H.; Alvarez, M. M.; Ant, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, K.; Whetten, R. L. J. Phys. Chem. 1999, 94, 8630-8633.
   1860 Hare, J. P.; Kroto, H. W.; Taylor, R. Chem. Phys. Lett. 1991, 177, 394-398.
   187 Reber, C.; Yee, L.; McKiernan, J. I.; Zink, J. L.; Williams, R. S.; Tong, N. W.; Ohlberg, D. A. A.; Whetten, R. L.; Diederich, F. N. J. Phys. Chem. 1991, 95, 2127-2129.
   188 Fruin, C. I.; Engleman, R.; Hedderich, H. G.; Bernath, P. F.; Lamb, L. D.; Huffman, D. R. Chem. Phys. Lett. 1991, 176, 504-507.

- (219) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Chiufollini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curle, R. F.; Smalley, R. E. J. Phys. Chem. 1990, 94, 8634-8636.
   (220) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarer, M. M.; Anz, S. J.; Whetten, R. L. J. Am. Chem. Soc. 1991, 113, 1050-1051.
   (221) Hawkins, J. M.; Lewis, T. A.; Loren, S. D.; Meyer, A.; Heath, J. R.; Shibato, Y.; Sayksily, R. J. J. Org. Chem. 1990, 55, 6250-6252.

- J. R.; Shibato, Y.; Saykally, R. J. J. Org. Chem. 1990, 55, 6250-6252.
   Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S. D.; Hollander, F. J. Science 1991, 252, 312-313.
   Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. J. Phys. Chem. 1991, 95, 11-12.
   Hare, J. P.; Dennis, T. J.; Kroto, H. W.; Taylor, R.; Allaf, A. W.; Balm, S. P.; Walton, D. R. M. J. Chem. Soc., Chem. Commun. 1991, 412-413.
   Sheltune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J.; Golden, W. G.; Seki, H.; Brown, C. A.; de Vrien, M. S. Chem. Phys. Lett. 1991, 179, 181-186.
   Bethune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J. Chem. Phys. Lett. 1990, 174, 219-222.
   Dennia, T. J.; Hare, J. P.; Kroto, H. W.; Taylor, R.; Walton, D. R. M.; Hendra, P. Spectrochimica Acta, in press.
   Johnson, R. D.; Meijer, G.; Bethune, D. S. J. Am. Chem. Soc. 1991, 113, 3619-3621.
   Tycko, R.; Haddon, R. C.; Dabbagh, G.; Glarum, S. H.; Douglass, D. C.; Mujace, A. M. J. Phys. Chem. 1991, 95, 518-520.
   Yannoni, Y. C. S.; Johnson, R. D.; Meijer, G.; Bethune, D. S.; Salem, J. R. J. Phys. Chem. 1991, 95, 212, 221, 221, 222, 223.

- Douglasa, D. C.; Mujace, A. M. J. Phys. Chem. 1991, 95, 518-520.

  (231) Yannoni, Y. C. S.; Johnson, R. D.; Meijet, G.; Bethune, D. S.; Salem, J. R. J. Phys. Chem. 1991, 95, 9-10.

  (232) Haddon, R. C.; Schneemeyer, I. F.; Waszczak, J. V.; Glarum, S. H.; Tyko, R.; Dabbagh, G.; Kortan, A. R.; Muller, A. J.; Mujace, A. M.; Rosseinsky, M. J.; Zahurak, S. M.; Makhija, A. V.; Thiel, F. A.; Raghavachari, K.; Cocknyne, E.; Elser, V. Nature (London) 1991, 350, 46-47.

  (233) Fowler, P. W. Nature 1991, 350, 20-21.

  (234) Wilson, R. J.; Meijer, G.; Bethune, D. S.; Johnson, R. D.; Chamblisa, D. D.; de Vries, M. S.; Hunziker, H. E.; Wendt, H. R. Nature (London) 1990, 348, 621-622.

  (235) Wragz, J. L.; Chamberlain, J. E.; White, H. W.; Krätschmer, W.; Huffman, D. R. Nature (London) 1990, 348, 623-624.

  (236) Chen, T.; Howells, S.; Gallagher, M.; Yi, L.; Sarid, D.; Lichenberger, D. L.; Nebesny, K. W.; Ray, C. D. Proceedings of Symposium G on Clusters and Cluster-Assembled Materials, Mater. Res. Soc. Proc. Averback, R. S., Nelson, D. L. Belland, R. S., Vickers, M.; Klinowski, J.; Hare, J. P.; Dennis, T. J.; Kröte, H. W.; Tsyler, R.; Welton, D. R. M. Unpublished results.
- lished results.

  (238) Fleming, R. M.; Siegrist, T.; Marsh, P. M.; Hessen, B.; Kortan, A. R.; Murphy, D. W.; Haddon, R. C.; Tyco, R.; Dabbagh.

Comment of the second

- Soc., Chem. Commun. 1991, in press.

  (239) Lichtenberger, D. L.; Nebesny, K. W.; Ray, C. D.; Huffman, D. R.; Lamb, L. D. Chem. Phys. Lett. 1991, 176, 203-208.

  (240) Lichtenberger, D. L.; Jatcho, M. E.; Nebesny, K. W.; Ray, C. D.; Huffman, D. R.; Lamb, L. D. Proceedings of Symposium G on Clusters and Cluster-Assembled Materials, Mater. Res. Soc. Proc.; Averback, R. S., Nelson, D. L., Bernholc, J., Eds.; MRS Publications: New York, 1991.

  (241) Luffer, D. R.; Schram, K. H. Rapid Commun. Mass Spectrometry 1990, 4, 552-556.

  (242) Proceedings of Symposium G on Clusters and Cluster-Assembled Materials, Mater. Res. Soc. Proc.; Averback, R. S., Nelson, D. L., Bernholc, J., Eds.; MRS Publications: New York, 1991.
- Neison, D. L., Bernholc, J., Eds.; MRS Publications: New York, 1991.

  (243) Herbst, E.; Klemperer, W. Astrophys. J. 1973, 185, 505-533.

  (244) Dalgarno, A.; Black, J. H. Rep. Prog. Phys. 1976, 39, 573-612.

  (245) Herbig, G. H. Astrophys. J. 1975, 195, 129-160.

  (246) Herbig, G. H. Astrophys. J. 1983, 331, 999-1003.

  (247) Snow, T. P.; Seab, C. G. Astron. Atrophys. 1989, 213, 291-294.

  (248) Somewille. W. B. Bellin, J. C. Mar. Not. B. 1989, 213, 201-294.

- 291-294.
   Somerville, W. B.; Bellis; J. G. Mon. Not. R. Astron. Soc. 1989, 240, 41P-46P.
   Léger, A.; d'Hendecourt, L.; Verstraete, L.; Schmidt, W. Astron. Astrophys. 1988, 20J, 145-148.

- (250) Joblin, C.; Mailard, J. P.; d'Hendecourt, L.; Léger, A. Nature 1990, 346, 729-731.

  (251) Hoyle, F.; Wickramsinghe, N. C. Astrophys. Space Sci. 1986. 122, 181-184.

  (252) Rabilizirov, R. Astrophys. Space Sci. 1986, 125, 331-339.

  (253) Wright, E. L. Nature (London) 1988, 336, 227-228.

  (254) Duley, W. W.; Williams, D. A. Mon. Not. R. Astron. Soc. 1988, 231, 969-975.

  (255) Léger, A.; Purch, L. J. Astron. Astrophys. 1984, 137, L5-L8.

  (256) Allamandola, L. J.; Tielena, A. G. G. M.; Barker, J. R. Astrophys. J. 1985, 230, 125-L28.

  (257) Balm, S. P.; Kroto, H. W. Mon. Not. R. Astron. Soc. 1990. 245, 193-197.

  (258) McKay, K. G.; Dunne, L.; Kroto, H. W. Manuscript in preparation.

  (259) Clayton, D. D. Nature (London) 1975, 257, 36-37.

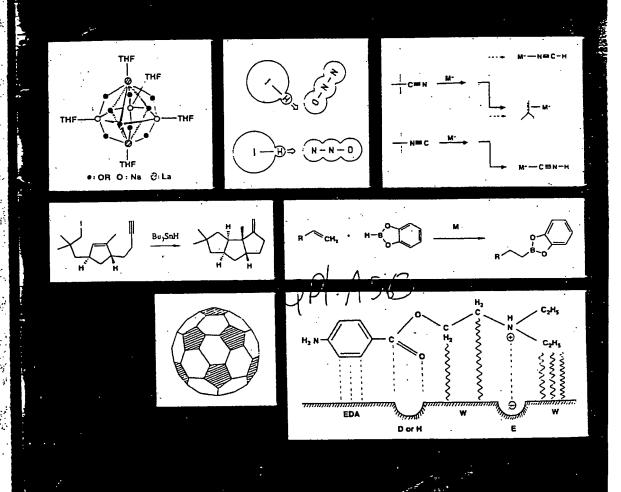
  (260) Zinner, E.; Wopenka, B.; Amari, S.; Anders, E. Lunar and Planetary Science XXI, 1991, in press.

  (261) Anderson, P. The Man-Kzin Warr, Niven, L., Eds.; Baen Publishing Enterprises, Simon and Schuster Distributors: New York, 1989, pp 168-169.

  (262) Vittal, J. J. Chem. Ed. 1989, 66, 282.

  (253) Diederich, F. N.; Foote, C. S.; Whetten, R. L. Chem. Eng. News 1991, in press.

## CHEMICAL REVIEWS



×

is usually such that all the fuel supply will pass to the engines by way of the main tank, which is refilled as necessary from the auxitiary tanks. In case of emergency, the system selector valve may connect the auxiliary tanks to the engines directly. If C.M./J.A.B.)

Diagram of a typical aircraft fuel system.

Fugacity A function introduced by G. N. Lewis to facilitate the application of thermodynamics to real systems. Thus, when fugacities are substituted for partial pressures in the mass action equilibrium constant expression, which applies strictly only to the ideal case, a true equilibrium constant results for real systems as well.

The fugacity  $f_i$  of a constituent i of a thermodynamic system is defined by the following equation (where  $\mu_i$  is the chemical

$$\mu_i \sim \mu_i^* + RT \ln f_i$$

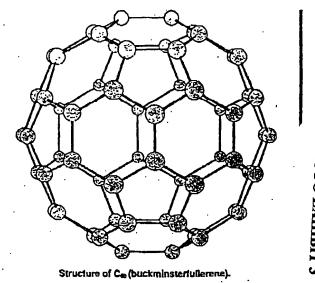
potential and  $\mu_1^*$  is a function of temperature only, in combination with the requirement that the fugacity approach the partial pressure as the total pressure of the gas phase approaches zero. At a given temperature, this is possible only for a particular value for  $\mu_1^*$ , which may be shown to correspond to the chemical potential the constituent would have as the pure gas in the ideal gas state at 1 atm pressure. This definition makes the fugacity identical to the partial pressure in the ideal gas case. For real gases, the ratio of fugacity to partial pressure, called the fugacity coefficient, will be close to unity for moderate temperatures and pressures. At low temperatures and appropriate pressures, it may be as small as 0.2 or less, whereas at high pressures at any temperature it can become very large. See Actumy (merimonymums); Chemical Equipment, Chemical Thermodynamics; Gas.

Fullerene A molecule containing an even number of carbon atoms arranged in a closed hollow cage. The fullerenes were discovered as a consequence of astrophysically motivated chemical physics experiments that were interpreted by using geodesic architectural concepts. Fullerene chemistry, a new field that appears to hold much promise for materials development and other applied areas, was born from pure fundamental science. See Carbon.

In 1985, fifteen years after it was conceived theoretically, the molecule buckminsterfullerene (C<sub>50</sub> or fullerene-60) was discovered serendipitously. Fullerene-60 (see illustration) is the archetypal member of the fullerenes, a set of hollow, closed-cage molecules consisting purely of carbon. The fullerenes can be considered, after graphite and diamond, to be the third well-defined allotrope of carbon.

In the fullerene molecule an even number of carbon atoms are arrayed over the surface of a closed hollow cage. Each atom is trigonally linked to its three near neighbors by bonds that delineate a polyhedral network, consisting of 12 pentagons and n hexagons. All 60 atoms in fullerene-60 are equivalent and lie on the surface of a sphere distributed with the symmetry of a truncated icosahedron. The 12 pentagons are isolated and interspersed symmetrically among 20 linked hexagons; that is, the symmetry is that of a modern soccerball. The molecule was named after R. Buckminster Fuller, the inventor of geodesic domes, which conform to the same underlying structural formula. Three of the four valence electrons of each carbon atom are involved in the sp2 sigma-bonding skeleton, and the fourth p electron is one of 60 involved in a pi-delocalized molecular-orbital electron sea that covers the outside (exc) and inside (endo) surface of the molecule. The resulting cloud of pi electron density is similar to that which covers the surface of graphite; indeed, the molecule can be considered a round form of graphite. See Electron configuration; Graphite

Fullerene-60 behaves as a soft electrophile, a molecule that readily accepts electrons during a primary reaction step. It can accept three electrons readily and perhaps even more. The molecule can be multiply hydrogenated, methylated, animonated; and fluorinated. It forms exchedral complexes in which an atom (or group) is attached to the outside of the cage, as well as endohedral complexes in which an atom [for example, lanthanum (La), potassium (K), or calcium (Ca)] is trapped inside the cage.

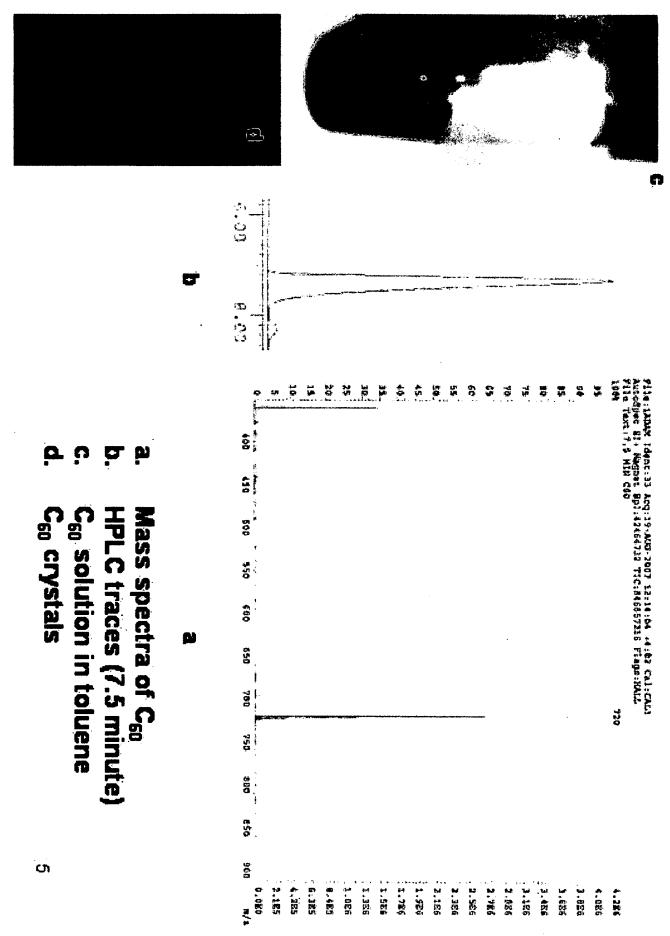


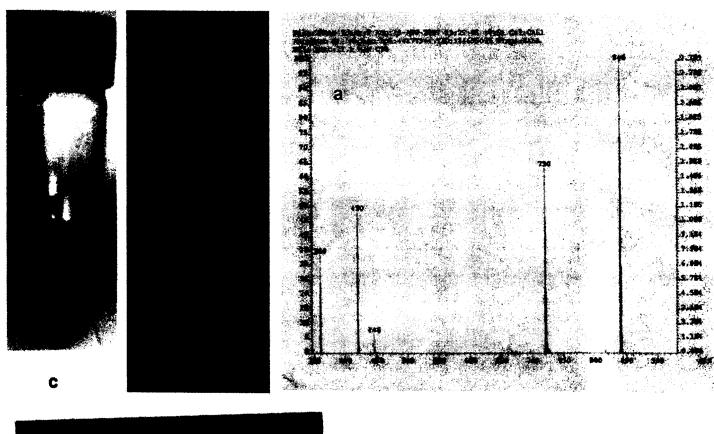
Fullerene materials have been available for such a short time that applications are yet to be established. However, the properties already discovered suggest that there is likely to be a wide range of areas in which the fullerenes or their derivatives will have uses.

-Fullerene-60 was discovered as a direct result of physicochemical investigations that simulated processes occurring in stars and in space. Consequently the likelihood that fullerenes, in particular fullerene-60, and analogs are present in space is a fascinating conjecture.

PLW.K.I

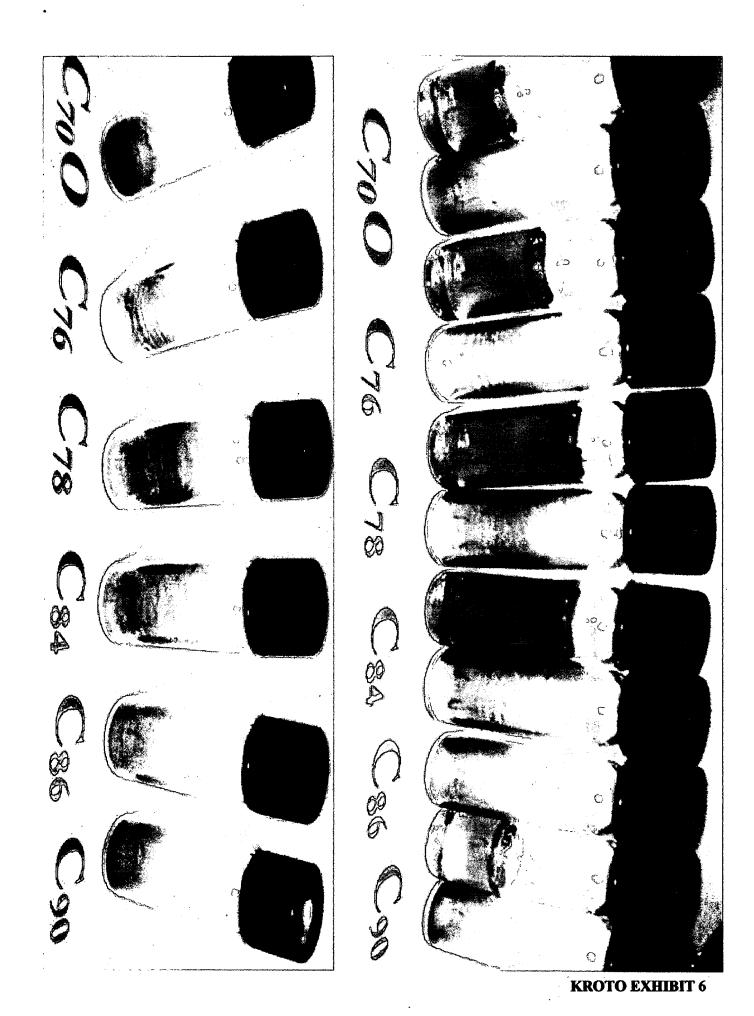
Fuller's earth Any natural earthy material (such as clay materials) which decolorizes mineral or vegetable oils to a sufficient extent to be of economic importance. It has no mineralogic significance. The clay minerals present in fuller's earth may include montmorillonite, attapulgite, and kaolinite.







- a. b.
- Mass spectra of  $C_{70}$ HPLC traces (11.1 minutes)  $C_{70}$  solution in toluene  $C_{70}$  crystals
- C.
- d.



# Mass spectra of C<sub>60</sub>

File:17ADAM Ident:9 Acq:25-AUG-2007 15:31:45 41:12 Cal:CALL AutoSpec Ei+ Magnet SpI:25737676 FIC:320138496 Flage:HALL File Text:C60/B3 5 5 HATE HATE HATE 60 in in 6 6 Ş 3 7 9 500 600 620 640 560 680 700 720 740 760 760 500 820 840 860 880 900 920 940 0.020 4.555 9.0ES 1.386 3.186 6.386 1.886 2.286 2,786 5.6E6 6.786 3,6E6 4.026 4.526 4.926 5.436 7. 2E6 7, 686 8.126 .8.586

8

## C<sub>60</sub> crystals C<sub>60</sub> solution in toluene

Ó



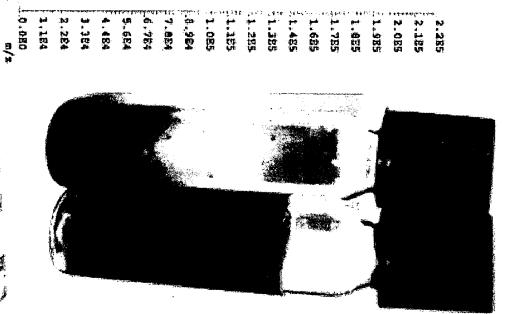
Mass spectra of C<sub>70</sub>

File:15ADAK ident:16 Acq:25-AUG-2607 15:22:03 +2:05 Cal:CAD1 AutoSpec Kl+ Magnet Bp:152497024 TiC:593336688 Flage:HALL File Text:C70 /82 0 45 <u>س</u>ا اف Ē Į. cy cy 60 10 O 840 350 1000 #/# C1.685 1.265 7, 3E 9.7E4 1.984 1,485 1. 725 3.954 5,924 1,925 2,155 2.385 2.585 2.785 3.525 3.765 2.985 3.185 1.385 

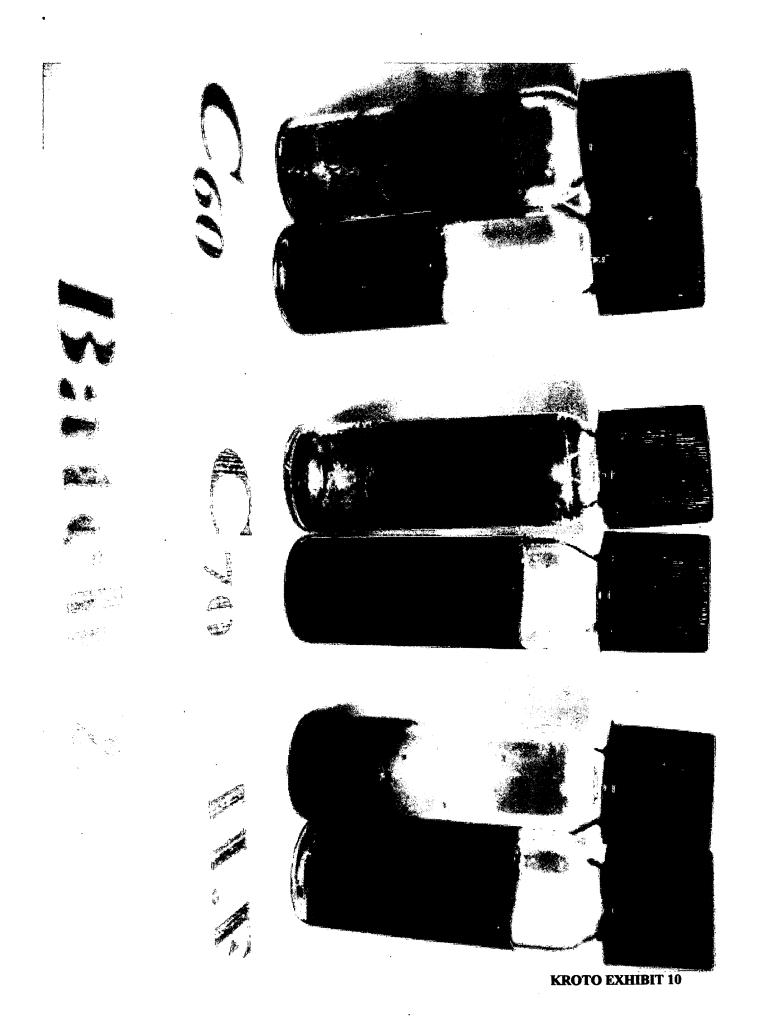
# C<sub>70</sub> solution in toluene C<sub>70</sub> crystals

File:13ADAM 1dent:22 Acq:25-AQQ-2007 15:05:52 +2:48 Cql:CAL1 AutoSpec EI- Magnet Bpl:50894484 TIC:863345472 Fiags:HALL File Text:HF/BA 85 75 15 \$ 5 8 8 Mass spectra of H.F's up to C<sub>104</sub> 1000 1050 1100 1150 **\$84** 150 1200 1250 1300 1350 1400

H.F's solution in toluene
H.F's crystals



**KROTO EXHIBIT 9** 



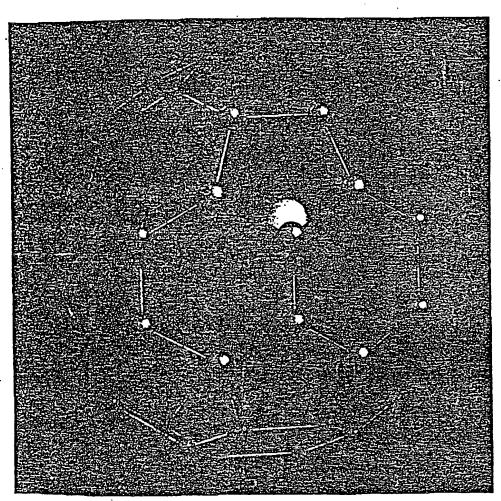
### SCIENTIFIC

OCTOBER 1991 53.95 L+S 10/1991

Remnants of a planet that falled to form.

Still no technological fix for oil spills.

What made higher life-forms possible?



Buckyball, the third form of pure carbon, cages an atom in its lattice.

### **Fullerenes**

These cagelike molecules constitute the third form of pure carbon (the other two are diamond and graphite). C60, the archetype, is the roundest molecule that can possibly exist

by Robert F. Curl and Richard E. Smalley

n May of 1990 Wolfgang Krätschmer and his student Konstantinos Fostiropoulos carefully mixed a few drops of benzene with a specially prepared carbon soot. The clear solvent

Excitedly, the two workers for the Max Planck Institute for Nuclear Physics in Heidelberg telephoned their colleborators, Donald Huffman and Lowell Lamb of the University of Arizona in Tueson, who quickly repeated the experiment. The excitement continued as the two groups communicated daily by telephone and fox, exchanging measurements of the material-its infrared and ultraviolet spectra, its X-ray diffraction pattern and its mass spectrograph. Yes, the values all matched those predicted for the 60-atom carbon cluster buckminsterfullerene.

Even though some theorists had argued that this bollow, soccerball-shaped molecule should be detectable in abundance in such everyday circumstances as a candle flame, the German-American team had actually found it, succeeding where all others had falled. They were the first to observe this roundest of all round molecules, and they knew that chemistry books and encyclopedias would never be quite the same. Now there were three known forms of pure carbon: the network solids, diamond and graphite, and a new class of discrete molecules—the fullerenes.

When we heard of this breakthrough a few months later in Tools, we cele-

ROBERT F. CURL and RICHARD E. SMALLEY of Rice University have collabcerated for the past seven years in research on carbon and semiconductor chasters in supersonic beams. Curi is a professor in, and chairman of, the department of chemistry. Smalley is the Gene and Norman Hackerman Professor of Chemistry and a professor of physics. For the past five years, he has also served as the chairman of the Rice Quanbrated, with champagne all around. For . although we had to some extent been scooped, we had been vindicated as well. Pive years earlier we had had our own Burekal experience. Together with our colleague Harold W. Kroto of the University of Sussex and our students James R. Heath and Sean C. O'Brien, we had found that Coo could be made in a uniquely stable form simply by laservaporizing graphite in a pulsed jet of heltum. We had gone on to propose that this extraordinary stability could be explained by a molecular structure having the perfect symmetry of a soccerball. Because the architectural principle also underlies the geodesic dome invented by the American engineer and philosopher R. Buckminster Puller, we named it buckminsterfullerene, or buckyball for short.

In addition to  $C_{40}$ , another molecule,  $C_{70}$ , appeared to be quite special in these early experiments. We soon found that the stability of C<sub>70</sub> could be under-stood if the molecule had also taken the form of a geodesic dome. As Fuller had pointed out, all such domes can be considered networks of pentagons and becagons. The 18th-century Swiss mathematician Leonhard Euler calculated that any such object must have precisely 12 pentagons in order to close into a spheroid, although the number of hexagons can vary widely. The soccerball structure of C<sub>20</sub> has 20 hexagons, whereas the structure we proposed for C<sub>20</sub> has 25, producing a shape reminiscent of a rugby ball.

in fact, we had found that all the even-numbered carbon clusters greater than about 32 atoms in size were remarkably stable (although less so than 60 or 70), and the evidence soon led us to postulate that all these molecules had taken the structure of geodesic domes. Again, in honor of Puller, it seemed fitting to term this entirely new class of molecules the fullerenea.

We later learned that such molecules had already been imagined. David E. H. Jones, writing under the pseudonym

"Daedahis" in the New Scientist in 1966, had conceived of a "hollow molecule" made of curied-up graphitic sheets. Others had predicted the stability of Con from calculations and tried-unsuccessfully-to synthesize it. We however, were apparently the first to discover that the material could form spontaneously in a condensing carbon vapor.

Although our evidence was sound and our conclusions were supported by extensive further experiments and theoretical calculations, we could not collect more than a few tens of thousands of these special new molecules. This amount was plenty to detect and probe with the sophisticated techniques available in our laboratory, but there was not enough to see, touch or smell. Our evidence was indirect, much as it is for physicists who study antimatter. For now, the fullerenes existed only as fleeting signals detected in our exotic machines. But as chemists, we knew that the new material ought to be parfectly stable. Unlike antimatter, the geodesic forms of carbon should be quite safe to hold in one's bare hand. All we had to do was make more of thembillions and billions more.

Thus, for five years, we had been searching for a method of producing visible amounts of the stuff. We called our efforts "the search for the yellow vial" because quantum calculations for such a soccerballshaped carbon molecule suggested it would absorb light strongly only in the far violet part of the spectrum. We were not alone. Our initial "soccerball"

HYPERFULLERENE STRUCTURE called a Russian egg is expected to form along with codinary fulleranes in a laser-vaporteel carbon plume. Shown here is the most symmetric form: a Can at the core is encapsulated by fullerenes having 240, 540 and 960 atoms. This process could continue indefinitely to produce a macroscopic particle whose pentagons are in joosahedral alignment.

tum hatitute.

proposal, published in *Nature* in 1985, had made the quest one of the hortest in chemistry.

In our laboratory we collected the sooty carbon produced by the vaporization laser while using various chemical techniques to detect the presence of Co. We shurried the soot in benzene, for example, and looked for a yellow color. But the solution in our test tubes stayed clear, with boring black soot sitting on the bottom. The community of cluster chemists ran many more sophisticated, experiments but achieved no better result.

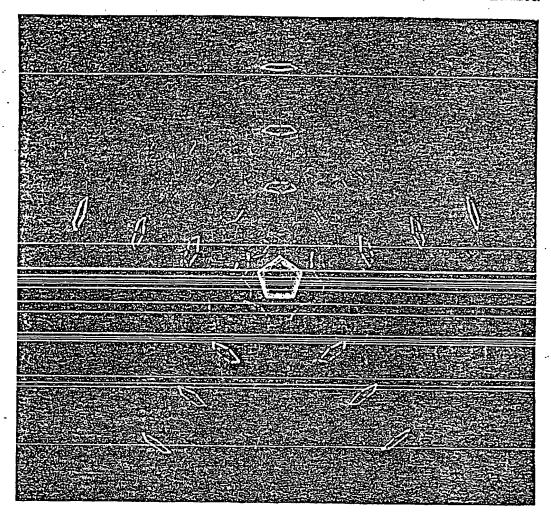
Many gave up hope of ever seeing the yellow vial. They reasoned that although the fullerenes may be stable, it was too hard to separate them from the other sooty material being produced in the vaporization experiments. Perhaps, the workers said, some dedicated chemist might one day extract a few micrograms with some special solvent, but no one seriously expected  $C_{\infty}$  to be available in bulk anytime soon.

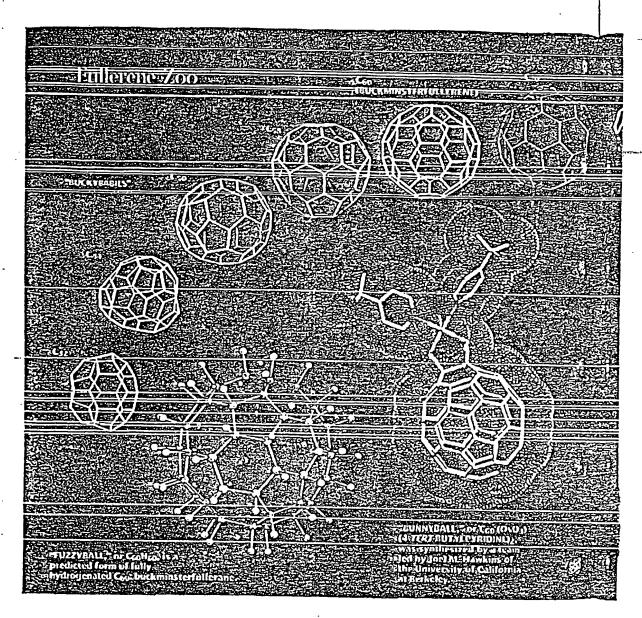
In the end, the breakthrough was made not by chemists but by physicists working in a totally different area. Huffman, Krätschmer and their students had been engaged for decades in a study of interstellar dust, which they assumed to consist mainly of particles of carbon (the most common particle-forming element). They therefore modeled the phenomenon in the laboratory by vaporizing carbon and condensing it in as many ways as possible. Optical tests figured in most of the studies. (Virtually all that is known of the interstellar dust stems from obser-

vations of how it absorbs and scatters starlight.)

In 1983 the physicists tried evaporating a graphite rod by resistive heating in an atmosphere of helium. They noticed that when the belium pressure was just right (about a seventh of an atmosphere), the dust strongly absorbed wavelengths in the far ultraviolet region, creating a peculiar, double-humped spectrum [see bottom Illustration on page 38). Most observers would have missed the two blips on the screen, but not Huffman and Krätschmer: they had studied spectra of carbon dust for years without encountering such an effect. They dubbed it their "camel" sample and wondered what it meant.

Nearly three years later, in the late fall of 1985, Huffman read in Nature of



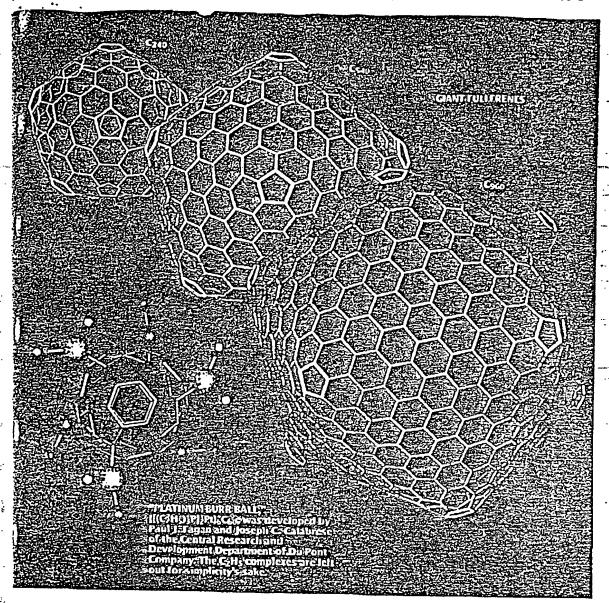


our discovery of  $C_{80}$  and began to wonder if a hollow soccerball molecule might be the cause of the double hump. Yet this explanation seemed too good to be true, for it required that  $C_{80}$  account for a significant portion of the sample. Why would so much of the carbon end up in such perfectly symmetric cages? What did the helium do to make it possible? The seeming unlikeliness of this hypothesis, together with some difficulty in reproducing the experiment, led the researchers to put the project on the back burner.

By 1989, however, Huffman and Krätschmer had become convinced that the C<sub>50</sub> hypothesis ought to be reexamined. They renewed their interest in the camel sample, readily reproducing the results of the 1983 experiments. This time their attention turned to measuring the sample's absorption of infrared light—the wavelengths that interact with the vibrational motion of molecules—in order to test the results against theoretical predictions that had by now been made for soccerball C<sub>60</sub>. These predictions held that of the 174

vibrational modes of this putative molecule, only 46 would be distinct, and only four would appear in the infrared range. To their surprise, they found the camel sample did display four sharp infrared absorption lines, and they verified that the lines were present only in carbon dust produced in the special camel way. This finding provided striking evidence that C<sub>60</sub> might be present in abundance.

influenced by their background in physics, the workers initially chose to test their hypothesis by a rather in-



volved route. They prepared a sample from pure <sup>13</sup>C, a heavy isotope of carbon, and verified that the extra mass shifted the four infrared bands in the way expected for so large a molecule composed exclusively of carbon. Ultimately, however, they realized that the simplest assay followed a basic dicrum of organic chemistry: like dissolves like. Should their sample dissolve in an aromatic solvent, such as benzene, this would support the predicted aromaticity of C<sub>ar</sub> Because benzene molecules take the shape of a ring of carbon at-

oms,  $C_{(a)}$  would thus be seen as a kind of spherical benzene.

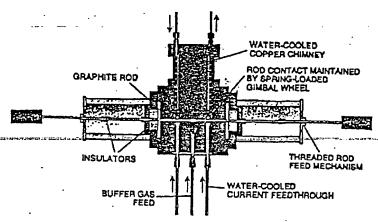
When the Krätschmer-Huffman group finally added benzene to their camel sample and saw the color red develop, they realized they were looking at the first concentrated solution of fullereness ever seen. They evaporated the solvent and found that tiny crystals remained, which readily redissolved. These crystals could be sublimed under a vacuum near 400 degrees Celsius and condensed on a cold microscope slide to form smooth films of solid materials,

which Kratschmer and Huffman christened "fullerite."

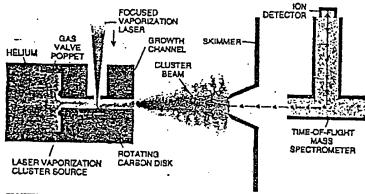
In thin layers these films were yellow (a fact that those of us at Rice University who searched for a "yellow vial" find highly gratifying). Although it took a while to obtain precise numbers, it is now known that carbon dust prepared in the camel way produces an extractable fullerene mixture made up of roughly 75 percent C<sub>10</sub> (the soccerball). 23 percent C<sub>n1</sub> (the rugby ball) and a grab bag of larger fullerenes.

Here was a new form of pure, solid

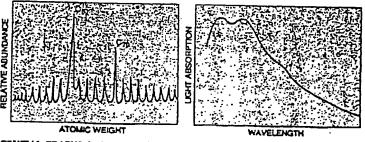
SCHNTTHE AMERICAN October 1991



FULLERENE FACTORY makes macroscopic samples in a carbon arc. The arc—a refinement of an apparatus developed by Wolfgang Krätschmer and Donald Huffman—frees carbon atoms that coalesce into sheets, linert belium holds the sheets near the arc long enough for them to close in on themselves, forming fullerenes.



CLUSTER GENERATOR designed by one of the authors (Smalley) produced the first evidence that fullerenes can form from carbon vapor. A pulsed laser vaporizes carbon; a gust of helium then sweeps the vapor into a supersonic beam whose expansion cools the atoms, condensing them.



CRUCIAL GRAPKS: in 1985 the cluster-beam generator aboved many even-minn-bered carbon clusters, especially C<sub>80</sub>, suggesting that these species are particularly stable. The humped ultraviolet absorption spectrum led Krätschmer and Huffman to dub it the "camel" sample; in 1990 it was shown to contain C<sub>80</sub>.

carbon. It is the only pure, finite form. The other two, diamond and graphite, are actually infinite network solids. In the real world, one usually deals with bunks of diamond cut out of larger bulk crystals. Under normal conditions, the surfaces of such a piece are instantly covered with hydrogen, which ties up the dangling surface bonds. Graphite is much the same. No piece of diamond, therefore, can ever be truly pure under normal conditions. The fullerenes, on the other hand, need no other atoms to satisfy their chemical bonding requirements on the surface. In this sense, the fullerenes are the first and only stable: forms of pure, finite carbon.

Once the Krätschmer-Huffman results were announced at a conference in Konstanz, Germany, in early September 1950, the race was on. The study of C<sub>50</sub> and the fullerenes had been the province of the few select groups that had something like our elaborate and expensive laser-vaporization cluster-beam apparatus. Now Krätschmer and Huffman had opened the field to anyone who could procure a thin rod of carbon, a cheap power supply, a bell-jar vacuum chamber and a few valves and gauges. Everybody could play,

ithin a few months, many groups were making their own fullerenes. Physicists, chemists and materials scientists thus began an interdisciplinary feeding frenzy that continues to intensify as this erticle is being written [sse box on page 62]. The key results have been quickly reproduced in over a dozen laboratories, some of which have applied alternative procedures of verification as well. Because fullerenes are readily soluble and vaporizable molecules that remain stable in air, they are perfectly suited to a wide range of techniques.

One of the most powerful techniques—nuclear magnetic resonance (NMR)—has confirmed the single most critical aspect of the soccerball structure: that all 60 carbon atoms have exactly the same relation to the whole. Only the truncated icosahedral structure we proposed for C<sub>50</sub> arranges the atoms so symmetrically as to distribute the strain of closure equally. Such even distribution makes for great strength and stability, indeed, that is why we proposed the structure in the first place: it explains the extraordinary stability of the 60-atom species.

Because C<sub>60</sub> is the most symmetric molecule possible in three-dimensional Euclidean space, it is literally the roundest of round molecules. Edgeless, chargeless and unbound, the molecule spins freely, as NMR experiments show,

more than 100 million times a second. The NMR experiments also dramatically verify that Cou has the shape of a tiny rugby ball: at room temperature, it spins rapidly about its long ads, stopping its frantic motion only below the temperature of liquid air.

High-resolution electron microscopy revealed these little carbon balls one at a time—as predicted, they spanned a bit more than one nanometer (a billionth of a meter). Scanning tunneling microscopy showed that when Co molecules are deposited on a crystalline surface, they pack as regularly as billiard balls. X-ray diffraction studies demonstrated thatas one would expect—C<sub>10</sub> crystallizes in a face-centered cubic lattice, with the balls a little more than 10 angstroms apart [see Illiustration on page 62]. The crystals are as soft as graphite. When squeezed to less than 70 percent of their initial volume, calculations predict that they will become even harder than diamond. When the pressure is relieved, they are observed to spring back to their normal volume. Thrown against steel surfaces at speeds somewhat greater than 17,000 miles per hour (about the orbital speed of the U.S. space shuttle), they are incredibly resilient: they just bounce tack.

We found that the most convenient way to generate fullerenes consists of setting up an are between two graphite electrodes. We maintained a constant gap by screwing the electrodes toward each other as fast as their tips evaporated. The process worked best when the hellum pressure was optimized and other gases, such as hydrogen and water vapor, were rigorously eluminated. Such measures produced yields of dissolvable fullerenes that typically ranged between 10 and 20 percent of the vaporized carbon. Yields as high as 45 percent have recently been reported.

The only irreducible cost appears to be that of the electricity needed to run the arc. But even the small bench-top generators we are now using in our labnratory provide electricity at a cost that amounts to only about five cents per gram of Cco. Recently it has been found that a sooting flame (such as that of a candle) can be used to produce substantial yields of Cor in the long run, this may prove the cheapest way to make the material. When the first large-scale applications of fullerenes are found-perhaps in superconductors. batteries or microelectronics [see box on page 62]—the manufacturing cost of City will probably fall close to that of aluminum: a few dollars a pound. What had recently been described as the "most controversial molecule in the

a bulk commodity:

host of questions arises out of this wonder. What exactly is the helium doing? How can such a perfectly symmetric molecule be formed with such high efficiency out of the chaos of a carbon arc? And, on a more personal level, where did we go wrong? Why did we, and all other chemists for that matter, fall in the search for the yellow vial? Our technique involved helium as well. What-did the Krätschmer-Huffman team do that made such a big difference?

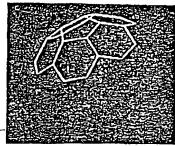
We now believe the answers to these questions lie in the way carbon vapor condenses at high temperatures. Linear carbon chains appear to link together to form graphitic sheets, and the sheets anneal as they grow in the hot vapor. Finally, stable, cagelike structures are favored by a key concept, which we call the pentagon rule.

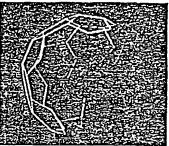
Scientists had long known that when carbon is vaporized, most of its atoms initially coalesce into clusters ranging from two to 15 atoms or so. The very smallest carbon molecules are known to prefer essentially one-dimensional geometries. But clusters containing at least 10 atoms most commonly form a monocyclic ring-a kind of molecular Hula-Hoop that is especially favored at low temperatures. At very high temperatures, the rings break open to form units that comprise as many as 25 curbon atoms, taking the form of linear chains. Such chains might be imagined to look something like writhing snakes as they vibrate in the hot vapor.

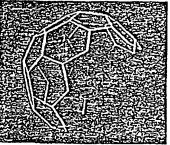
It was these linear carbon chains that initially got us involved in carbon cluster studies and led to the discovery of Ceo. Our British colleague, Harry Kroto. had theorized that the great abundance of such linear carbon chains in interstellar space may arise from chemical reactions in the outer atmospheres of carbon-rich red giant stars, in the early 1980s one of us (Smalley) had developed a supersonic cluster-beam device for the general study of small clusters composed of essentially any element in the periodic table [see "Microclusters," by Michael A. Duncan and Dennis H. ROUVIEY: SCIENTIFIC AMERICAN, December 1989l.

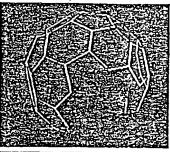
We produced clusters by focusing an intense pulsed laser on a solid disk of the element to be studied. The local temperature could readily be brought above 10.000 degrees C-hotter than the surface of most stars and certainly hot enough to vaporize any known material. The resulting vapor was entrained in a powerful gust of helium, a chemi-

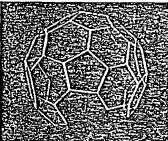
### Cosmos" is well on its way to becoming Growth of a Buckyball











cally inert carrier gas, which roused the vapor so that it could condense into small clusters. As the carrier gas expanded through a nozzle into a vacuum, it generated a supersonic beam of chisters whose sizes could be measured by a mass spectrometer.

in 1984 a group at Doon using a copy of the cluster-beam apparatus developed at Rice had been the first to study carbon clusters in this fashion. Their results strongly suggested that the linear carbon chains Kroto wanted to study were in fact being produced in abundance. In addition, they reported a bizzere pattern among the larger clusters: the distribution was strikingly lacking in the species having an odd number of atoms.

The Exon researchers recorded but did not notice that two particular even-numbered members, C<sub>50</sub> and C<sub>70</sub>, were somewhat more abundant than their neighbors [see bottom illustration on page 58]. The mysterious even-numbered distribution of chisters was separated from the small linear-chain distribution by what appeared to be something of a forbidden zone—a region of chisters between roughly 25 and 35 atoms in size in which few if any clusters could be detected.

he even-numbered distribution was soon discovered to result from the fullerenes. In one of our many studies of Kroto's lineer carbon chains, we reproduced the Exxon results but found something quite striking about the distribution of large, even-numbered clusters. Heath, Kroto and O'Brien noticed that the 60th cluster seemed five times more abundant than any other even-numbered cluster in the range between 50 and 70 atoms. This differential was dramatically greater than anything that had been seen before.

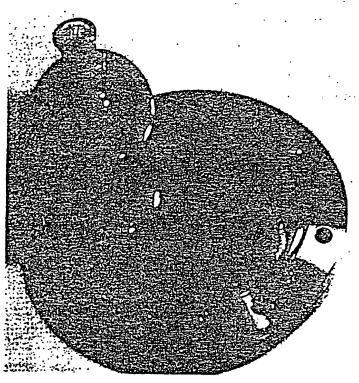
After much discussion, Heath and O'Brien spent the next weekend playing with the conditions in the laser-vaporization machine's supersonic nozzle. By Monday morning they had managed to find conditions in which Costood out in the cluster distribution like a flagpole. By the next morning we had had our Eurekai experience, and we were playing with every sort of soccerball we could get our hands on.

We found that we could explain the dominance of the even-numbered clusters by assuming they had all taken the attracture of hollow, geodesic domes. They were all fullerenes. We could also argue that some fullerenes were more abundant than others because of the amoothness of the clusters' surface and the natural grouping of pentagons.

Pentagons provided an important clue. Although hundreds of examples are known in chemistry of five-membered rings attached to six-membered rings attached to six-membered rings attached to six-membered rings attached to six-membered rings attached for example, the nucleic acids adenine and guanine), only a few occur whose two five-membered rings share an edge interestingly, the smallest fullerene in which pentagons need not share an edge is C<sub>90</sub>; the next is C<sub>90</sub>. Although C<sub>10</sub> and all larger fullerenes can easily adopt attructures in which the five-membered rings are well separated, one finds that these pentagons in the larger fullerenes occupy strained post-

tions. This vulnerability makes the carbon atoms at such sites particularly susceptible to chemical attack.

The hig question, however, was not why fullerenes were stable but rather how they formed so readily in laser-vaporized graphite. Near the end of 1985, we suggested that the process began with linear chains. As the carbon vapor began to condense, the linear chains would grow long enough to filip back on themselves to form large monocyclic Hula-Hoops. As the growth continued, the chains would also fold into more effectively connected polycyclic network structures. Because graphite,



COLOR OF  $C_{80}$  depends on its form. This yellow film was sublimed onto a glass window that had been boiled to a vacuum oven. The benzene solution is magenta.



FULLERENE CRYSTALS were produced by evaporating a benzene solution of  $C_{\Theta}$  containing a significant admixture of  $C_{\Theta}$ :

the most stable known form of carbon, has its atoms bound in infinite hexagonal sheets, we suspected that the polycyclic network clusters resembled pieces of such sheets. We expected it to look like a fragment of chicken wire.

Like a cutout section of chicken wire,

these graphitic sheets would have many dangling bonds, making them chemically reactive—much more so than the smaller linear chains, which have only two such bonds, one on each end. The sheets, therefore, would not be expected to be abundant in the cluster beams.

Almost as soon as they form, they react with other small carbon molecules and grow too large to be seen. This, we believe, explains why there is a forbidden zone between the small linear-chain distribution and the first small fullerenes.

Chemists are conditioned to think of

### Fullerene Electronics

erties of bulk Coo are electronic: in various compound forms it functions as an insulator, a conductor, a semiconductor and a superconductor.

The material crystallizes when C<sub>60</sub> molecules pack together like Ping-Pong balls in a face-centered cubic lattice. Calculations over the past few months have predicted that this new material is a direct band-gap semiconductor like gallium arsenide. All its units stand precisely at their posts in a crystalline structure. But unlike the elements of gallium arsenide, the buckyballs spin freely and at random. This disorder gives them a certain resemblance to amorphous silicon—a constituent of inexpensive solar cells. The peculiar disorder within order of bulk C<sub>60</sub> has yet to be fully explored, but it is expected to produce a wholly new kind of-semiconductor.

Early In 1991 researchers at AT&T Bell Laboratories discovered that they could mix, or dope,  $C_{60}$  with potassium to produce a new metallic phase—a "buckide" sait. It reaches its maximum electrical conductivity when there are three potassium atoms to each buckyball. If too much potassium is added, however, the material becomes insulating. Subsequent work has shown that  $K_1C_{60}$  is a stable metallic crystal consisting of a face-centered cubic structure of buckyballs, with potassium ions filling the cavities between the balls. Potassium buckide is the first completely three-dimensional molecular metal.

The Bell Labs team further discovered that this K<sub>3</sub>C<sub>40</sub> metal becomes a superconductor when cooled below 18 kelvins. When rubidium is substituted for the potassium, the critical temperature for superconductivity was found to be near 30 keiwins. (Recently workers at Allied-Signal, Inc., detected superconductivity at 43 kelvins for rubidium-thallium-doped material.) Careful work at the University of California at Los Angeles has shown that the superconducting phase is stable and readily annealed—imperfections can be smoothed away by heating and cooling.

 $\mathbb{E}(H^{k}) \cong \mathbb{E}_{\mathbb{R}}$ 

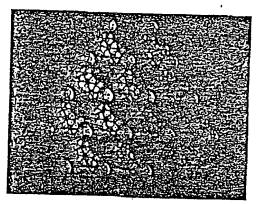
The material can therefore be manufactured as a threedimensional superconductor, making it a candidate for practical superconducting wires. Early estimates of magnicial and other characteristics indicate that these superconducting buckide salts are similar to the high-temperature superconducting ceramics made of yttrium, barium and copper oxide.

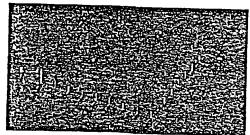
Recent work at the University of Minnesota has shown that highly ordered  $C_{60}$  films can readily be grown on crystalline substrates, such as galilum arsenide. This attribute makes the film a suhable material for microelectronic fabrication. Beautifully regular films of the  $K_1C_{60}$  superconductor can also be made [see micrograph at right], and the interface between the  $C_{60}$  crystalline film and the  $K_1C_{60}$  material has been found to be stable. It may thus lend itself to the production of intricately layered microelectronic devices.

In order for the semiconducting properties of fullerene materials to be thoroughly exploited, scientists need to

learn how to dope them selectively to make n-type and p-type fullerene films, which donate electrons and holes, respectively. Such doping may involve putting a dopant atom inside the cage, either by growing the cage around the atom or by shooting atoms through the carbon walls by brute force. Small atoms, such as helium, have aiready been injected this way into the C<sub>10</sub> cage, and it seems likely that hydrogen and lithium are insertable as well.

The versatility of bulk  $C_{60}$  seems to grow week by week. As we go to press, for example, there is a report suggesting that fullerene complexes exhibit ferromagnetic qualities in the absence of metals, an unparelleled phenomenon. Also, British workers from the universities of Leicester. Southampton and Sussex have just reported the generation of macroscopic quantities of fully fluorinated buckyballs ( $C_{60}F_{60}$ ). The resulting "teflon balls" may be among the world's best jubricants. We do not know what the fullerenes' burgeoning traits will allow, but it would be surprising if the possibilities are not wonderful.

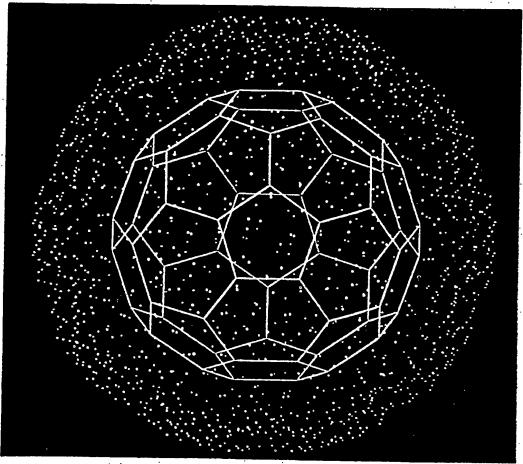




SUPERCONDUCTING FULLERIDE forms when buckyballs are doped with potassium in the ratio of  $K_1C_m$  (diagram), producing a crystal that can be grown on a gallium arsenide substrain (scanning tunneling micrograph).

### 12 CULT C INTERNATIONAL WEEKLY JOURNAL OF SCIENCE

Volume 318 No 6042 14-20 November 1985 £190



### SIXTY-CARBON CLUSTER

### **AUTUMN BOOKS**

Harvey Brooks (transformation of MIT) P. N. Johnson-Laird

(brain and mind)
Anthony W. Clare

(psychoanalysis as religion)

A. O. Lucas (war on disease) Hendrik B. G. Casimir (physics and physicists)

Gordon Thompson (dimensions of nuclear proliferation)

Jacques Ninio (origins of life)

Edward Harrison (steps through the cosmos)

### Ca: Buckminsterfullerene

H. W. Kroto", J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Teras 77251, USA

During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells', graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The Complecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

The technique used to produce and detect this unusual molecule involves the vaporization of carbon species from the surface of a solid disk of graphite into a high-density helium flow, using a focused pulsed laser. The vaporization laser was the second harmonic of Q-switched Nd:YAG producing pulse energies of -30 mJ. The resulting carbon clusters were expanded in a supersonic molecular beam, photoionized using an excimer laser, and detected by time-of-flight mass spectrometry. The vaporization chamber is shown in Fig. 2. In the experiment the pulsed valve was opened first and then the vaporization laser was fired after a precisely controlled delay. Carbon species were vaporized into the helium stream, cooled and partially equilibrated in the expansion, and travelled in the resulting molecular beam to the ionization region. The clusters were ionized by direct one-photon excitation with a carefully synchronized excimer laser pulse. The apparatus has been fully described previously<sup>2-5</sup>

The vaporization of carbon has been studied previously in a very similar apparatus. In that work clusters of up to 190 carbon atoms were observed and it was noted that for clusters of more than 40 atoms, only those containing an even number of atoms were observed. In the mass spectra displayed in ref. 6, the  $C_{60}$  peak is the largest for cluster sizes of >40 atoms, but it is not completely dominant. We have recently re-examined this system and found that under certain clustering conditions the  $C_{60}$  peak can be made about 40 times larger than neighbouring clusters.

Figure 3 shows a series of cluster distributions resulting from variations in the vaporization conditions evolving from a cluster. distribution similar to that observed in ref. 3, to one in which Cso is totally dominant. In Fig. 3c, where the firing of the vaporization laser was delayed until most of the He pulse had passed, a roughly gaussian distribution of large, even-numbered clusters with 38-120 atoms resulted. The Ceo peak was largest but not dominant. In Fig. 3b, the vaporization laser was fired at the time of maximum helium density; the Cro peak grew into a feature perhaps five times stronger than its neighbours, with the exception of C70. In Fig. 3a, the conditions were similar to those in Fig. 3b but in addition the integrating cup depicted in Fig. 2 was added to increase the time between vaporization and expansion. The resulting cluster distribution is completely dominated by Coo. in fact more than 50% of the total large cluster abundance is accounted for by Ceo; the Cro peak has diminished in relative intensity compared with C<sub>60</sub>, but remains rather prominent, accounting for -5% of the large cluster population. Our rationalization of these results is that in the laser vaporization, fragments are torn from the surface as pieces of the planar

Fig. 1. A football (in the United States, a soccerball) on Texas grass. The Camolecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by acarbon atom.



graphite fused six-membered ring structure. We believe that the distribution in Fig. 3c is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most stable species, which appears to be a unique cluster containing 60 atoms.

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise from a graphite fragmentation, this result seems impossible: there is not much to choose between such isomers in terms of stability. If one tries to shift to a tetrahedral diamond structure, the entire surface of the cluster will be covered with unsatisfied valences. Thus a search was made for some other plausible structure which would satisfy all sp2 valences. Only a spheroidal structure appears likely to satisfy this criterion, and thus Buckminster Fuller's studies were consulted (see, for example, ref. 7). An unusually beautiful (and probably unique) choice is the truncated icosahedron depicted in Fig. 1. As mentioned above, all valences are satisfied with this structure, and the molecule appears to be aromatic. The structure has the symmetry of the icosahedral group. The inner and outer surfaces are covered with a sea of w electrons. The diameter of this Coo molecule is ~7 Å, providing an inner cavity which appears to be capable of holding a variety of atoms".

Assuming that our somewhat speculative structure is correct, there are a number of important ramifications arising from the existence of such a species. Because of its stability when formed under the most violent conditions, it may be widely distributed in the Universe. For example, it may be a major constituent of circumstellar shells with high carbon content. It is a feasible constituent of interstellar dust and a possible major site for

Paperitation laser



Fig. 2 Schematic diagram of the pulsed supersonic nozzle used to generate carbon cluster beams. The integrating cup can be removed at the indicated line. The vaporization laser beam 100-40 mJ at 532 nm in a 5-ns pulse1 is focused through the nozzle, striking a graphine disk which is rotated slowly to produce a smooth vaporization surface. The pulsed nozzle passes high-density helium over this vaporization zone. This helium carrier gas provides the thermalizing collisions necessary to cool, react and cluster-the species in the vaporized graphite plasma, and the wind necessary to carry the cluster products through the remainder of the nozzle. Free expansion of this cluster-laden gas at the end of the nozzle forms a supersonic beam which is probed 1.3 m downstream with a time-of-flight mass spectrometer.

Permanent address: School of Chemistry and Molecular Sciences, University of Sussess, Brighton BNI 9QI, UK

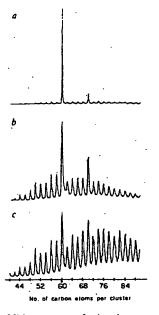


Fig. 3 Time-of-flight mass spectra of carbon clusters prepared by laser vaporization of graphite and cooled in a supersonic beam. ionization was effected by direct one-photon excitation with an ArF excimer laser (6.4 eV, 1 mJ cm<sup>-2</sup>). The three spectra shown differ in the extent of helium collisions occurring in the supersonic nozzle. In c, the effective helium density over the graphite target-was less than 10 torr-the observed cluster distribution here is believed to be due simply to pieces of the graphite sheet ejected in the primary vaporization process. The spectrum in b was obtained when roughly 760 torr helium was present over the graphite target at the time of laser vaporization. The enhancement of  $C_{60}$  and  $C_{70}$  is believed to be due to gas-phase reactions at these higher clustering conditions. The spectrum in a was obtained by maximizing these cluster thermalization and cluster-cluster reactions in the 'integration cup' shown in Fig. 2. The concentration of cluster species in the especially stable  $C_{\infty}$  form is the prime experimental observation of this study.

surface-catalysed chemical processes which lead to the formation of interstellar molecules. Even more speculatively,  $C_{00}$  or a derivative might be the carrier of the diffuse interstellar

If a large-scale synthetic route to this Co species can be found, the chemical and practical value of the substance may prove extremely high. One can readily conceive of C60 derivatives of many kinds—such as  $C_{60}$  transition metal compounds, for example,  $C_{60}$ Fe or halogenated species like  $C_{60}$ Fe which might be a super-lubricant. We also have evidence that an atom (such as lanthanum and oxygen) can be placed in the interior, producing molecules which may exhibit unusual properties. For example, the chemical shift in the NMR of the central atom should be remarkable because of the ring currents. If stable in macroscopic, condensed phases, this Cas species would provide a topologically novel aromatic nucleus for new branches of organic and inorganic chemistry. Finally, this especially stable and symmetrical carbon structure provides a possible catalyst and/or intermediate to be considered in modelling prebiotic chemistry.

We are disturbed at the number of letters and syllables in the rather fanciful but highly appropriate name we have chosen in the title to refer to this Ceo species. For such a unique and centrally important molecular structure, a more concise name would be useful. A number of alternatives come to mind (for example, ballene, spherene, soccerene, carbosoccer), but we prefer to let this issue of nomenclature be settled by consensus.

We thank Frank Tittel, Y. Liu and Q. Zhang for helpful discussions, encouragement and technical support. This research was supported by the Army Research Office and the Robert A. Welch Foundation, and used a laser and molecular beam apparatus supported by the NSF and the US Department of Energy. H.W.K. acknowledges travel support provided by SERC, UK. J.R.H. and S.C.O'B. are Robert A. Welch Predoctoral Fellows.

### Received 13 September; accepted 18 October 1985,

- Henth, J. R. *et al.* Astrophys. J. Isubmitted).
   Dietz, T. G., Dancan, M. A., Powers, D. E. & Smalley, R. E. J. chem. Phys. 74, 6511-6512 (1971).
   Powers, D. E. et al. J. phys. Chem. 84, 2356-2360 (1982).
   Powers, D. E. et al. J. phys. Chem. 84, 2356-2360 (1982).
   Hopkins, J. B., Longridge-Smith, P. R. R., Moras, M. D. & Smalley, R. É. J. chem. Phys. 78, 1627-1637 (1983).
   C'Briten, S. C. et al. J. chem. Phys. (submitted).
   Robling, E. A., Cax, D. M. & Kaldor, A. J. chem. Phys. 81, 3322-3330 (1984).
   Marth, R. W. The Dymanion World of Buckmister Fuller (Reinhold, New York, 1960).
   Heath, J. R. et al. J. Am. Aberts, Soc. (in the press).
   Herath, J. R. et al. J. Am. Aberts, Soc. (in the press).
   Herath, J. R. et al. J. Am. Aberts, Soc. (in the press).
   Herath, J. R. et al. J. Am. Aberts, Soc. (in the press).
   Herath, J. R. et al. J. Am. Aberts, Soc. (in the press).



### The Nobel Prize in Chemistry 1996

"for their discovery of fullerenes"

Press release

The Fullerene Gallery

Robert F. Curl, Jr.

TISA

Rice University Houston, USA

1933 -

Autobiography



Sir Harold W. Kroto

U.K.

University of Sussex, Brighton, U.K.

1939 -

Autobiography





Richard E. Smalley

USA

Rice University, Houston, USA

1943 -

Autobiography

- Copyright© 1999 The Nobel Foundation
- . For help, info, credits or comments, see "About this project"
- Last updated by Webmaster@www.nobel.se / June 3, 1999

10/15/1999 11:0

**KROTO EXHIBIT 13** 



Press Release: The 1996 Nobel Prize in Chemistry

### KUNGL. VETENSKAPSAKADEMTEN THE ROYAL SWEDISH ACADEMY OF SCIENCES

- 9 October 1996 - ---

The Royal Swedish Academy of Sciences has decided to award the 1996 Nobel Prize in Chemistry to

Professor Robert F. Curl, Jr., Rice University, Houston, USA, Professor Sir Harold W. Kroto, University of Sussex, Brighton, U.K., and Professor Richard E. Smalley, Rice University, Houston, USA,

for their discovery of fullerenes.

Note: This document is made for Netscape 2.0 or later, and some of the chemical formulas might not appear as intended using other browsers.

### The discovery of carbon atoms bound in the form of a ball is rewarded

New forms of the element carbon - called fullerenes - in which the atoms are arranged in closed shells was discovered in 1985 by Robert F. Curl, Harold W. Kroto and Richard E. Smalley. The number of carbon atoms in the shell can vary, and for this reason numerous new carbon structures have become known. Formerly, six crystalline forms of the element carbon were known, namely two kinds of graphite, two kinds of diamond, chaoit and carbon(VI). The latter two were discovered in 1968 and 1972.

Fullerenes are formed when vaporised carbon condenses in an atmosphere of inert gas. The gaseous carbon is obtained e.g. by directing an intense pulse of laser light at a carbon surface. The released carbon atoms are mixed with a stream of helium gas and combine to form clusters of some few up to hundreds of atoms. The gas is then led into a vacuum chamber where it expands and is cooled to some degrees above absolute zero. The carbon clusters can then be analysed with mass spectrometry.

Curl, Kroto and Smalley performed this experiment together with graduate students J.R. Heath and S.C. OBrien during a period of eleven days in 1985. By fine-tuning the experiment they were able in particular to produce clusters with 60 carbon atoms and clusters with 70. Clusters of 60 carbon atoms,  $C_{60}$ , were the most abundant. They found high stability in  $C_{60}$ , which suggested a molecular structure of great symmetry. It was suggested that  $C_{60}$  could be a "truncated icosahedron cage", a polyhedron with 20 hexagonal (6-angled) surfaces and 12 pentagonal (5-angled) surfaces. The pattern of a European football has exactly this structure, as does the geodetic dome designed by the American architect R. Buckminster Fuller for the 1967 Montreal World Exhibition. The researchers named the newly-discovered structure buckminsterfullerene after him.

10/15/1999 11:01

The discovery of the unique structure of the  $C_{60}$  was published in the journal *Nature* and had a mixed reception - both criticism and enthusiastic acceptance. No physicist or chemist had expected that carbon would be found in such a symmetrical form other than those already known. Continuing their work during 1985-90, Curl, Kroto and Smalley obtained further evidence that the proposed structure ought to be correct. Among other things they succeeded in identifying carbon clusters that enclosed one or more metal atoms. In 1990 physicists W. Krātschmer and D.R. Huffman for the first time produced isolable quantities of  $C_{60}$  by causing an arc between two graphite rods to burn in a helium atmosphere and extracting the carbon condensate so formed using an organic solvent. They obtained a mixture of  $C_{60}$  and  $C_{70}$ , the structures of which could be determined. This confirmed the correctness of the  $C_{60}$  hypothesis. The way was thus open for studying the chemical properties of  $C_{60}$  and other carbon clusters such as  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$  and  $C_{84}$ . New substances were produced from these compounds, with new and unexpected properties. An entirely new branch of chemistry developed, with consequences in such diverse areas as astrochemistry, superconductivity and materials chemistry/physics.

### Background

Many widely diverse research areas coincide in the discovery of the fullerenes. Harold W. Kroto was at the time active in microwave spectroscopy, a science which thanks to the growth of radioastronomy can be used for analysing gas in space, both in stellar atmospheres and in interstellar gas clouds. Kroto was particularly interested in carbon-rich giant stars. He had discovered and investigated spectrum lines in their atmospheres and found that they could be ascribed to a kind of long-chained molecule of only carbon and nitrogen, termed cyanopolyynes. The same sort of molecules is also found in interstellar gas clouds. Kroto's idea was that these carbon compounds had been formed in stellar atmospheres, not in clouds. He now wished to study the formation of these long-chain molecules more closely.

He got in touch with Richard E. Smalley, whose research was in cluster chemistry, an important part of chemical physics. A cluster is an aggregate of atoms or molecules, something in between microscopic particles and macroscopic particles. Smalley had designed and built a special laser-supersonic cluster beam apparatus able to vaporise almost any known material into a plasma of atoms and study the design and distribution of the clusters. His paramount interest was clusters of metal atoms, e.g. metals included in semiconductors, and he often performed these investigations together with Robert F. Curl, whose background was in microwave and infra-red spectroscopy.

### Atoms form clusters

When atoms in a gas phase condense to form clusters, a series is formed where the size of the clusters varies from a few atoms to many hundreds. There are normally two size maxima visible in the distribution curve, one around small clusters and one around large. It is often found that cer-tain cluster sizes may dominate, and the number of atoms in these is termed a "magic number", a term borrowed from nuclear physics. These dominant cluster sizes were assumed to have some special property such as high symmetry.

### Fruitful contact

Through his acquaintanceship with Robert Curl, Kroto learned that it should be possible to use Smalley's instrument to study the vaporisation and cluster formation of carbon, which might afford him evidence that the long-carbon-chain compounds could have been formed in the hot parts of stellar atmospheres. Curl conveyed this interest to Smalley and the result was that on 1 September 1985 Kroto arrived in Smalley's laboratory to start, together with Curl and Smalley, the experiments on carbon vaporisation. In the course of the work it proved possible to influence drastically the size distribution of the carbon clusters where, predominantly, 60 appeared as a magic number but also 70 (Fig. 1). The research group

. 10/15/1999 11:01

now got something else to think about. Instead of long carbon chains, the idea arose that the C<sub>60</sub> cluster could have the structure of a truncated (cut off) icosahedron (Fig. 2) since its great stability was assumed to correspond to a closed shell with a highly symmetrical structure. C<sub>60</sub> was given a fanciful name, buckminsterfullerene, after the American architect R. Buckminster Fuller, inventor of the geodesic dome. This hectic period ended on 12 September with the despatch of a manuscript entitled  $C_{so}$ Buckminsterfullerene to Nature. The journal received it on 13 September and published the article on 14 November 1985.

### Sensational news.

For chemists the proposed structure was uniquely beautiful and satisfying. It corresponds to an aromatic, three-dimensional system in which single and double bonds alternated, and was thus of great theoretical significance. Here, moreover, was an entirely new example from a different research tradition with roots in organic chemistry: producing highly symmetrical molecules so as to study their properties. The Platonic bodies have often served as patterns, and hydrocarbons had already been synthesised as tetrahedral, cubic or dodecahedral (12-sided) structures.

### Carbon atoms per cluster

Fig. 1 Using mass spectroscopy it was found that the size distribution of carbon clusters could be drastically affected by increasing the degree of chemical "boiling" in the inlet nozzle to the vacuum chamber. Models of the structures of  $C_{60}$ . (Acc. Chem. Res., Clusters with 60 and 70 carbon atoms could be produced. (Acc. Chem. Res., Vol. 25, No. 3, 1992)

Fig. 2 Vol. 25, No. 3, 1992)

### Further investigations

To gain further clarity Curl, Kroto and Smalley continued their investigations of  $C_{60}$ . They attempted to make it react with other compounds. Gases such as hydrogen, nitrous oxide, carbon monoxide, sulphur dioxide, oxygen or ammonia were injected into the gas stream, but no effect on the  $C_{60}$  peak recorded in the mass spectrometer could be demonstrated. This showed that  $C_{60}$  was a slow-reacting compound. It also turned out that all carbon clusters with an even number of carbon atoms from 40-80 (the interval that could be studied) reacted equally slowly. Analogously with  $C_{60}$  all these should then correspond to entirely closed structures, resembling cages. This was in agreement with Euler's law, a mathematical proposition which states that for any polygon with n edges, where n is an even number greater than 22, at least one polyhedron can be constructed with 12 pentagons and (n-20)/2 hexagons, which, in simple terms, states that it is possible with 12 pentagons and with none or more than one hexagon to construct a polyhedron. For large n many different closed structures can occur, thus also for  $C_{60}$ , and it was presumably the beautiful symmetry of the proposed structure that gave it the preference:

The combination of chemical inertia in clusters with even numbers of carbon atoms and the possibility that all these could possess closed structures in accordance with Euler's law, led to the proposal that all these carbon clusters should have closed structures. They were given the name fullerenes and conceivably an almost infinite number of fullerenes could exist. The element carbon had thus assumed an almost infinite number of different structures.

### C<sub>60</sub> and metals

New experiments were rapidly devised to test the  $C_{60}$  hypothesis. Since the  $C_{60}$  structure is hollow, with room for one or more other atoms, attempts were made to enclose a metal atom. A graphite sheet was soaked with a solution of a metal salt (lanthanum chloride, LaCl<sub>3</sub>) and subjected to vaporisation-condensation experiments. Masspectroscopic analysis of the clusters formed showed the presence of  $C_{60}$ La<sup>+</sup>. These proved to be photoresistant, i.e. irradiation with intense laser light did not remove the metal atoms. This reinforced the idea that metal atoms were captured inside the cage structure.

The possibility of producing clusters with a metal atom enclosed gave rise to what was termed the "shrink-wrapping" experiment. Ions of one and the same size or at least similar sizes were gathered in a magnetic trap and subjected to a laser pulse. It then turned out that the laser beam caused the carbon cage to shrink by 2 carbon atoms at a time: at a certain cage size, when the pressure on the metal atom inside

10/15/1999 11:0:

became too great, the fragmentation ceased. The shell had then shrunk so that it fitted exactly around the metal atom. For  $C_{60}Cs^+$  this size was at  $C_{48}Cs^+$ , for  $C_{60}K^+$  it was at  $C_{44}K^+$  and for  $C_{60}^+$  at  $C_{32}^+$ .

Further strong evidence gave rise to new chemistry

At the end of the 1980s, strong evidence was available that the  $C_{60}$  hypothesis was correct. In 1990 the synthesis of macroscopic quantities of  $C_{60}$  through carbon arc vaporisation between two graphite electrodes permitted the attainment of full certainty - the whole battery of methods for structure determination could be applied to  $C_{60}$  and other fullerenes and completely confirmed the fullerene hypothesis. As opposed to the other forms of carbon the fullerenes represent well-defined chemical compounds with in some respects new properties. A whole new chemistry has developed to manipulate the fullerene structure, and the properties of fullerenes can be studied systematically. It is possible to produce superconducting salts of  $C_{60}$ , new three-dimensional polymers, new catalysts, new materials and electrical and optical properties, sensors, and so on. In addition, it has been possible to produce thin tubes with closed ends, nanotubes, arranged in the same way as fullerenes. From a theoretical viewpoint, the discovery of the fullerenes has influenced our conception of such widely separated scientific problems as the galactic carbon cycle and classical aromaticity, a keystone of theoretical chemistry. No practically useful applications have yet been produced, but this is not to be expected as early as six years after macroscopic quantities of fullerenes became available.

### Further reading

Jim Baggott, Perfect Symmetry: The Accidental Discovery of Buckminsterfullerene, Oxford University Press, 1994, IX + 315 pp.

Hugh Aldersey-Williams, *The Most Beautiful Molecule: An Adventure in Chemistry*, Aurum Press, London, 1995, IX + 340 pp.

Robert F. Curl and Richard E. Smalley, Probing C<sub>60</sub>, Science, 18 Nov. 1988 Vol. 242

Harold Kroto, Space, Stars, C<sub>60</sub>, and Soot, Science, 25 Nov. 1988 Vol. 242

H.W. Kroto, A.W. Allaf, and S.P. Balm,  $C_{60}$ : Buckminsterfullerene, American Chemical Society, 1991

Richard E. Smalley, Great Balls of Carbon; The Story of Buckminsterfullerene, The Sciences, March/April 1991

The All-Star of Buckyball; Profile: Richard E. Smalley, Scientific American, September 1993 Rudy M. Baum, Commercial Uses of Fullerenes and Derivatives Slow to Develop, News Focus, Nov. 22, 1993 C&EN

Hargittai, Istv(SIGMA)n, Discoverers of Buckminsterfullerene, The Chemical Intelligencer, Springer-Verlag, New York, 1995

Robert F. Curl Jr., was born in 1933 in Alice, Texas, USA: Ph.D. in chemistry in 1957 at University of California, Berkeley, USA. Curl has since 1958 worked at Rice University, where he has been a professor since 1967.

Professor Robert F. Curl Jr. Department of Chemistry Rice University P.O. Box 1892 Houston, TX 77251, USA

Sir Harold W. Kroto was born in 1939 in Wisbech, Cambridgeshire, UK. He obtained his Ph.D. in 1964

10/15/1999 11:01

at the University of Sheffield, U.K. In 1967 he moved to the University of Sussex, where he still works. In 1985 he became Professor of Chemistry there and in 1991 Royal Society Research Professor.

Professor Sir Harold W. Kroto School of Chemistry and Molecular Sciences University of Sussex Brighton, Sussex BN1 9QJ, UK

Richard E. Smalley was born in 1943 in Akron, Ohio, USA. Ph.D. in chemistry 1973 at Princeton University, USA. Professor of Chemistry at Rice University since 1981 and also Professor of Physics at the same university since 1990. Member of the National Academy of Sciences in the USA and other bodies.

Professor Richard E. Smalley Department of Chemistry Rice University P.O. Box 1892 Houston, TX 77251, USA

• Copyright© 1999 The Nobel Foundation
• For help, info, credits or comments, see "About this project"
Last updated by Webmaster@www.nobel.se / November 30, 1998

# IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Donald R. Huffman, et al.

Examiner:

Tsang Foster, S.N.

Serial No.:

08/236,933

Art Unit:

1745

Filed:

May 2, 1994

Docket:

7913ZAZY

For:

NEW FORM OF CARBON

Confirmation No.: 4115

Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

# DECLARATION OF MAURICIO TERRONES PURSUANT TO 37 C.F.R. §1.132

Sir:

I, MAURICIO TERRONES, declare and say as follows:

1. I am a full professor at the Instituto Potosino de Investigación Científica y
Tecnológica (IPICyT) in San Luis, Potosí, Mexico. I was awarded a Ph.D. at the University of
Sussex, England in 1997 where I did my doctoral studies under the supervision of Professor
Harold W. Kroto. For over 10 years, I have been conducting research in carbon nanoscience and
nanotechnology. I have written over 176 articles in prestigious journals in the areas of carbon
nanostructures and nanoscience and technology, and I have given several oral presentations on
these subjects. Further, I have received several awards for my research work. For the
convenience of the United States Patent and Trademark Office, I have attached hereto as Exhibit
1 my curriculum vitae, describing my credentials and expertise in the area of fullerenes and
carbon nanostructures and carbon nanoscience and technology.

- 2. In preparing this Declaration, I have read and reviewed the contents of USSN 08/236,933 ("'933 application"), especially the description therein of the preparation of fullerenes, including C<sub>60</sub> and C<sub>70</sub>, and especially Examples 1-3 thereof.
  - 3. I was introduced to applicants' attorney by Dr. Harold W. Kroto.
- 4. I was requested by applicants' attorney to prepare fullerenes, including C<sub>60</sub> and C<sub>70</sub>, by repeating the experiments described in the '933 application utilizing the same apparatus and conditions as described therein. In particular, I was asked by applicants' attorney to prepare the fullerenes by following the procedure in the '933 application at two different pressures, viz, at 100 torr and 2 atm, using a current of 100 amps.
- 5. Dr. Kroto coordinated the research on behalf of the applicants. He instructed me to prepare the soot by the techniques described in the '933 application. In an effort to meet the time requirements of the United States Patent and Trademark Office, I was instructed to forward the soot produced from the vaporization of graphite at 100 torr and at 2 atm to Dr. Adam Darwish, whom I understand would carry out the separation of the fullerenes from the soot.
- 6. I note that the bell jar apparatus described in the '933 application is no longer available or being used to produce fullerenes. In order to perform the experiments as described in the '933 application, I had to rebuild a bell jar apparatus in order to make it operational. Further, I adapted an aluminum chamber for high pressure experiments by replacing the glass container of the bell jar with an aluminum container in order to provide for safe operation at the increased pressure of 2 atmospheres, in accordance with the description in the '933 application.
- 7. The construction of the apparatus and the set-up of the experiments for the preparation of the soot, and the experiments performed using the bell jar apparatus and

aluminum reactor, as described in this Declaration, were either conducted by me or were conducted under my direct supervision and control.

- 8. The bell jar apparatus which was built was identical to the one described in the '933 application. However, it had one constraint. It could only be used to vaporize carbon for about 2 minutes and then had to be cooled down (for a few minutes) before another run could be conducted. In addition, the glass container of the bell jar was not thick enough and did not have proper stoppers for conducting high-pressure experiments. Therefore and in order to conduct the vaporization of graphite at the higher pressures of 2 atmospheres, as described in Paragraph 6, I modified the bell jar apparatus by replacing the glass cover of the bell jar apparatus with an aluminum chamber, which was adapted with stoppers and bolts/nuts to keep the aluminum cover in place for high pressure operation (hereinafter this modified bell jar apparatus with an aluminum cover will be referred to as an "aluminum reactor"). This aluminum reactor was equivalent to the bell jar apparatus described in the '933 application; moreover, the aluminum reactor had the same constraints as those described hereinabove with respect to the bell jar apparatus. Thus, the vaporization of the graphite to form the soot was conducted for no longer than about 2 minutes at the lower pressure and for considerably less time at the higher pressure. In fact, the vaporization at 2 atm was performed in two or three segments, each no longer than about 25 sec. These short operation times for high pressure experiments were performed to guarantee stable pressures during the graphite vaporization experiments.
- 9. The soot was produced in accordance with the procedure described in the '933 application, especially Examples 1 and 2 therein. Accordingly, 1 gram of soot was produced by performing several runs at the lower pressure; about 100 mg., on average, of soot was obtained from each run.

10. The procedure for preparing the soot at 100 torr was performed in accordance with the description in the '933 application. The following is a general procedure for each run.

Graphite rods were heated via resistive heating in a bell jar, which was evacuated to 10<sup>-4</sup> torr and then filled with high purity helium. The system was evacuated three times before filling the chamber with helium. Pure graphite rods of ½ inch in diameter were utilized. The length of each rod varied, generally ranging from about 3 to 4 cm; moreover, a one-centimeter length of the tip of each rod was reduced in diameter to about 5 millimeters. The graphite rods were evaporated by resistive heating at 100 torr helium using a current of 100 amps.

The graphite rods were heated under resistive heating for about 2 minutes. The vapor was collected on a substrate, an aluminum sheet (used as a collector) in a semicircular configuration, which was placed about 4.7 cm from the bottom of, 7.57 cm to the right of, and 11 cm from the top of, the evaporating carbon rods. The bell jar apparatus was opened after the cooling down period of 20 minutes, and the black soot thus formed was removed by scraping the soot from the substrate surfaces and internal surfaces of the bell jar apparatus.

Generally about 100 mg. of soot, on average, were collected from each run. This was repeated until 1 gram of soot was collected, and the soot was forwarded to Dr. Adam Darwish for separation of the fullerenes therefrom.

- 11. Photographs of the set-up of the bell jar apparatus are attached hereto as Exhibit 2.
- 12. In order to produce the soot at the higher pressure, the procedure outlined in Paragraph 10 was repeated, except the pressure was raised to 2 atm. In addition, as indicated hereinabove, the aluminum reactor described above was utilized in lieu of the bell jar apparatus. The procedure is outlined below.

13. The graphite rods were vaporized in the aluminum reactor that had been evacuated to 10<sup>-4</sup> torr and then filled with high purity helium. The entire system was evacuated three times before it was filled with helium.

Graphite rods of ¼ inch in diameter were utilized but they had a longer length of about 10.2 cm at the cathode and 4.7 cm at the anode. A one-centimeter length at the tip of each rod was reduced in diameter to 5 millimeters.

The graphite rods were vaporized via resistive heating at 2 atm under a current of 100 amps for about 1 minute, divided into three time periods: 25 seconds, 13 seconds, and 22 seconds. The vapor was collected on a substrate (aluminum sheet in semi circle), which was placed about 4.7 cm below, 7.57 cm to the right of, and 11 cm on top of, the evaporating carbon rods. The evaporator was opened after the cool down period of 20 minutes, and the black soot was removed by scraping the soot from the substrate surfaces and the internal surfaces of the aluminum reaction. Approximately 100 mg. of soot was collected.

- 14. In order to meet the time constraints imposed by the United States Patent and Trademark Office, there was no attempt to amass the soot at the higher pressure to obtain a large amount of soot, as performed for the lower pressure experiments.
- 15. Photographs of the set up at the higher pressure of 2 atm are attached hereto as Exhibit 3.
- 16. The soot produced at the higher pressure was also forwarded to Dr. Adam Darwish for separation of the fullerenes therefrom.
- 17. I further declare that all statements made herein of my own knowledge are true and that alls statements made on information and belief are believed to be true and further that these statements were made with the knowledge that willful false statements and the like so

made are punishable by fine or imprisonment or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: 28 AUGUST 2007

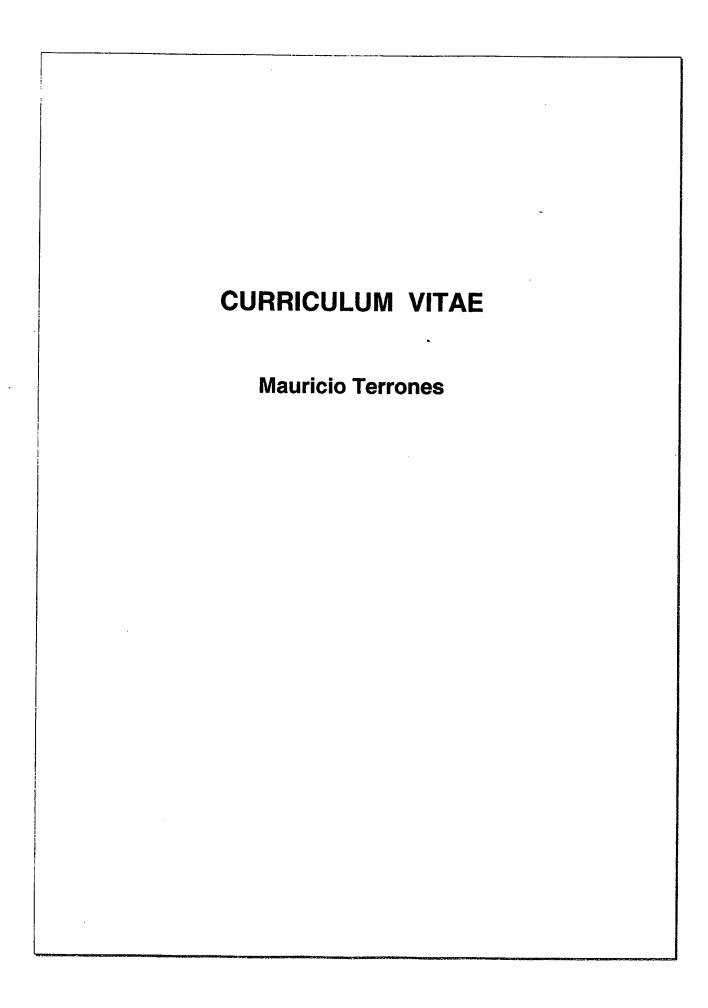
Mauricio Terrones, Ph.D.

Mauricio Terrones is a native of Mexico City born in 1968, obtained his B.Sc. degree in Engineering Physics at Universidad Iberoamericana (1992, Mexico City). He received the highest grade point average (GPA) award and the highest recognition for his B.Sc. Thesis ("Mención Honorífica"). In that year, he was also awarded a Medal for being one of the best students of México (a recognition given by the Mexican President). After lecturing at Universidad Iberamericana for two years, in 1993 he was awarded a Fulbright fellowship to carry out doctoral studies in the USA. However, he did not take this fellowship and preferred to travel to the UK and work for a Ph.D. with Prof. Harold W. Kroto (Nobel Prize Winner in Chemistry 1996). He pursued his graduate studies fully sponsored by CONACYT-Mexico. In 1997, he obtained his doctorate degree and started to work as a postdoctoral research fellow at the University of Sussex. After a postdoctoral year, funded by the Materials Research Laboratory (UC-Santa Barbara) and the Royal Society, he was appointed Research Fellow at the Fullerene Science Centre and was funded by the Royal Society.

In 1999, Mauricio Terrones returned to Mexico and became a faculty member as Assistant Professor "category A", at the Institute of Physics -UNAM (Mexico). In 1999, he was also awarded an Alexander von Humboldt Fellowship to carry out research at the Max-Planck-Institut für Metallforschung in Stuttgart (Germany). In April 2001, he became full Professor (category "C") at the Instituto Potosino de Investigación Científica y Tecnológica (IPICYT). Mauricio Terrones has co-authored more than 175 publications in prestigious international journals such as Nature (3), Science (3), Nature Nanotechnology (1), Physical Review Letters (9), Nano Letters (16), Chemical Physics Letters (35), Annual Reviews of Materials Research (1), Advanced Materials (6), International Materials Reviews (1), etc. He has been awarded the UNESCO Javed Husain Prize for Young Scientists and received the Albert Einstein Medal in November 2001 for his numerous contributions in Carbon Nanoscience and Nanotechnology. In 2001, he also received the National Prize for Chemistry in Mexico for his work on Carbon Nanoscience. His work has also been recognized by various agencies and Magazines in Mexico (e.g. Mexican Achievers 2004, Top 30 outstanding young people by "Revista Expansión", Outstanding Young Mexicans by "Revista Dia Siete", etc). In 2005, he received the José Antonio Villaseñor prize (a recognition given by the State government of San Luis Potosi) for his contribution to the production of N-doped carbon nanotubes and his applications. In that year, he was also awarded the TWAS prize (given by the Academy of Sciences for the Developing World) in Engineering for his outstanding contributions to the synthesis and characterization of novel carbon-based nano-materials. Mauricio Terrones is the youngest scientist ever to win a TWAS Prize. In 2005, we was elected member of the TWAS. In April 2006, he was awarded by UNAM the "Fernando Alba" medal for his outstanding contributions to experimental physics.

The scientific impact and quality of his publications has given him more than 3500 independent citations (without auto-citations) in international journals and books. In addition, he has co-edited a special issue on Nanoscience and Nanotechnology of Carbon that was published in November 2004 by Philosophical Transactions (The Royal Society). He has also written 8 book chapters, 2 independent reviews, 19 articles in conference proceedings and 6 miscellaneous publications. He has presented his research in more than 90 international conferences. The average impact factor of his publications is >4, according to the Institute for Scientific information 1998. He has been invited to present his research in more than 60 international conferences (i.e. England, Austria, USA, Hungary, Belgium, Argentina, Brazil, Chile, Korea, Germany, Japan, etc.) devoted to nanotubes.

Mauricio Terrones is one of the most productive scientists in Mexico, and has closely participated in the creation of the first Fullerene and Nanotube Laboratory in Mexico (Departamento de Física Aplicada y Tecnología Avanzada, UNAM). He has set-up the new Nanoscience Laboratory at IPICYT and is now leader of the National Laboratory for Nanoscience and Nanotechnology Research (LINAN), recently approved by CONACYT-Mexico.



# **Professor Mauricio Terrones**

Potosí Institute of Science and Technology (IPICYT)

Camino a la Presa San Jose 2055 C.P. 78216, San Luis Potosí, Mexico Home Tel: +52 (444) 825-6596

Work Tel: +52 (444) 834-2039; Fax: +52 (444) 834-2040 e-mail: mterrones@ipicyt.edu.mx

#### I. PERSONAL DATA

Date of Birth:

28 November 1968.

Place of Birth:

Mexico City.

Nationality:

Mexican.

Marital Status

Married (Elizabeth FLORESGOMEZ); Son (Diego TERRONES)

Address

Cordillera Occidental 760; Depto. 4

Col. Lomas 4<sup>8</sup>. Sección

San Luis Potosí, SLP. C.P. 78216

**Telephone Number** 

++52 (444) 825-65-96

### II. EDUCATION

1997

Ph.D. University of Sussex, England

Major: Chemical-Physics

Thesis: "Production and Characterisation of Novel Fullerene-related

Materials: Nanotubes, Nanofibres and Giant Fullerenes".

Thesis Supervisors: Prof. H. W. Kroto, FRS (Nobel Laureate), Dr. D. R.

Walton, FRSC

1992

Licenciatura (B.Sc. by Thesis) Universidad Iberoamericana, México City,

México.

Grade Point Average: 9.62/10
Major: Engineering Physics
Minor: Thermo-Fluids

Thesis: "Parametric Study of a Photochemical Reaction Modelled by an

Integro-Differential Reaction Diffusion Equation".

Thesis Supervisors: Dr. Leopoldo García Colin Sherer, Dr. Guillermo

Terrones.

1984

High School. Universidad La Salle, México City, México.

**Grade Point Average: 9.92/10** 

1981

Junior High School (Junior High School). Instituto Ingles Mexicano,

México City, México.

Grade Point Average: 9.6/10

1975

Elementary School (Elementary School). Instituto Ingles Mexicano.

México City, México.

Grade Point Average: 9.4/10

#### III. EXPERIENCE

#### Research

Apr. 2001-

Full Professor (Tenure) at the Instituto Potosino de Investigación Científica y

present	Tecnológica IPICYT (San Luis Potosí, México).
Apr. 2004 Jun. 2004	Invited professor Université Catholique de Louvain la Neuve & Université de Namur, Belgium (April 2004 – June 2004).
Jan. 2004 Mar. 2004	Visiting Director of the International Center for Young Scientists (ICYS) at the National Institute of Materials Science (NIMS), Japan.
Oct. 1999- Dec. 2000	Alexander von Humboldt Fellowship tenable at the Max Planck Institut für Metallforschung (Stuttgart). Research Programme entitled: "Structural and dynamic behaviour of metals encapsulated in nested fullerenes and nanotubes".
Mar. 1999- Mar. 2001	Associate Professor at the Institute of Physics - UNAM-Mexico. Department of Applied Physics and Advanced Technology (Queretaro, Mexico).
Jun. 1999- present	Associate Research Fellow at Birkbeck College - Department of Crystallography (University of London). Structural Caracterisation of nanomaterials.
Jan. 1999- Jun. 1999	Research Fellow at the University of Sussex sponsored by the Royal Society. Research Programme entitled: "Novel graphite-like structures" under the supervision of H. W. Kroto (FRS).
Nov 1997- Dec. 1998	Research Fellow at the Fullerene Science Centre sponsored by the Materials Research Laboratory (University of California Santa Barbara) and the Royal Society. Controlled production of nanomaterials and applications.
Jul. 1997- Oct. 1997	Research Fellow (Fullerene Science Centre) at the School of Chemistry, Physics and Environmental Sciences, University of Sussex. Nanotubes and other forms of Carbon.
Jan. 1994- Jun.1997	School of Chemistry, Physics and Environmental Sciences, University of Sussex. Application of molecular simulations, and diffraction and spectroscopic techniques to the physico-chemical study of fullerenes, nanotubes and new graphitic structures.
Jan. 1991- Dec. 1993	Department of Physics, Universidad Iberoamericana Asymptotic analysis to determine the existence of travelling wave solutions in a single step photochemical reaction. Finite difference methods for non- linear parabolic-type partial differential equations.
Teaching	
Aug. 1992- Dec. 1993	Profesor de Asignatura ( <u>Instructor</u> ) Department of Physics: Universidad Iberoamericana.  Teaching the following freshman courses (1st. and 2nd. year):  * <u>Mechanics</u> (Theory and Laboratory)  * <u>Thermodynamics</u> (Theory and Laboratory)  * <u>Continuum Mechanics</u> (Theory)  * <u>Electricity and Magnetism</u> (Laboratory).
Jan. 1992- Dec. 1993	Profesor de Asignatura ( <u>Instructor</u> ) Department of Mechanical Engineering, Universidad Iberoamericana. Thermodynamics Engineering (Laboratory).

May 1992	Design of new experiments for instruments for instructional purposes for the following laboratories: Electricity and Magnetism, Mechanics and Thermodynamics Engineering.
Jan. 2001 Mar. 2001	Lecturer in Physical Chemistry at the University of Sussex – Department of Chemistry, Physics and Environmental Science (UK). Teaching Modern Materials (3 <sup>rd</sup> year undergraduate).
Aug. 2002- Dec. 2003	Advanced Materials Department (IPICYT), Teaching: Tópicos Avanzados de Materiales I Investigación Doctoral I
Jan. 2003- Jun. 2003	Advanced Materials Department (IPICYT), Teaching: Tópicos Avanzados de Materiales II Investigación Doctoral I Investigación Doctoral II
Aug. 2003- Dec. 2003	Advanced Materials Department (IPICYT), Teaching: Materiales Nanoestructurados y Laboratorio Tópicos Avanzados de Materiales I Investigación Doctoral I Investigación Doctoral III
Jan. 2004- Jun. 2004	Advanced Materials Department (IPICYT), Teaching: Temas Selectos de Ciencias Físicas Investigación Doctoral II Investigación Doctoral III Investigación Doctoral IV
Jan. 2004- May. 2004	Profesor de Asignatura ( <u>Instructor</u> ) Department of Physics and Mathematics. Universidad Iberoamericana. Teaching courses (3 <sup>rd</sup> & 4 <sup>th</sup> year): * <u>Física de Materiales</u> (Theory)
Aug. 2004- Dec. 2004	Advanced Materials Department (IPICYT), Teaching: Materiales Nanoestructurados y Laboratorio Tópicos Avanzados de Materiales I Investigación Doctoral V Investigación Doctoral VI

### PhD Students (Graduated)

 Julio Alejandro Rodríguez Manzo. (Ph.D. IPICYT, México). Title: "Magnetismo un Nanoestructras de Carbono y Cuasicristales". Termination February 2007.

 Benjamín Fragneud (Ph.D. IPICYT, México) Title: "Síntesis y Caracterización de Materiales Compuestos Polímero/Nanotubo de Carbono: Impacto del Injerto de Polímero a la Superficie de los CNx MWNTs sobre las Propiedades Eléctricas y Mecánicas de los nano-compuestos". Thesis writen in English. Termination December 2006.

 J. Jesús Velásquez Salazar (Ph.D. IPICYT, México) Title: "Síntesis y Caracterización de Nanotubos por molienda mecánica". Termination November 2006.

 Eduardo Terrés Rojas (Ph.D. IPICYT, México) Title: "Síntesis, Caracterización y propiedades electrónicas y catalíticas de Nanomateriales porosos de carbono". Termination October 2006.

5. Adalberto Zamudio Ojeda. (Ph.D. IPICYT, México). Title: "Síntesis y

Caracterización de Nanoestructuras de Carbono y Anclaje de Nanopartículas de Plata en Nanotubos de Carbono: Teoría y Experimento". Termination September 2006.

 Ana Laura Elías Arriaga (Ph.D. IPICYT, México) Title: "A Multidisciplinary Study of Carbon Nanotube Structures: From Inorganic to Biological Systems". Thesis writen in English. Termination July 2006.

 Felipe Valencia Hernández (Ph.D. IPICYT, México) Title: "Stability of Curved and Highly Starined Carbon Nanostructures and their interaction with laser excitatcion".

Thesis writen in English. June 2005.

 Marisol Reyes Reyes. (Ph.D. UNAM and IPICYT, México). Title: "Microscopía Electrónica y estudio Experimental de nanoalambres de carbono". Date of Exam 12<sup>th</sup> November 2003.

 Torsten Seeger (Ph.D., Max-Planck Institut für Metallforschung, Germany). Title: "Synthesis and characterization of model composites made of multiwall nanotubes and SiO₂". October 2001. Co-supervsion with Prof. Manfred Rühle.

### Masters and Undergraduate students (Graduated)

 Xavier Lepró (M.Sc. IPICYT, México). Title: "Attachment of Transition Metal Nanoparticles on Nitrogen Doped Carbon Nanotubes (MWNTs-CNx) and their Further Reactions". Thesis written in English. Termination September 2006.

 Jalme Enrique Pérez Terrazas (M.Sc. IPICYT, México). Title: "Estudios Estructurales de C₀₀ Polimerizado mediante tratamiento de presión y Temperatura

usando dinámica molecular". Thesis written in English. Termination July 2005.

 Pedro Armando Ojeda May (M.Sc. IPICYT, México). Title: "Determinación de la Quiralidad de Nanotubos mediante la Función de Distribución Radial (RDF) y Algoritmo de Crecimiento para Fullerenos". Thesis written in English. Termination April 2005.

- Daniel Ramírez González. (B.Sc by thesis, IPICYT, México) Title: "Novel Properties
  of Ferromagnetic Nanowires: Theory and Experiment". Received degree Nov. 2002.
- Federico Villalpando Páez (B.Sc. Universidad Iberoamericana, México). Title: "Carbon Nanotubes: Theory and Experiment". Degree Received August 2003.
- Mariela Bravo Sánchez. (B.Sc by thesis, IPICYT, México) Title: "Electronic Properties of Non-classical Fullerenes using Hueckel Approximations". Degree to be received in December 2003.
- Giles Middleton (B.Sc. (project student), University of Sussex, UK). Title: "Production and purification of carbon nanotubes and metal nanowires". Received degree Jul. 1999.
- Claran Cahil (B.Sc. (project student), University of Sussex, UK). Title: "Generation of aligned nanotube films via self-assembly processes". Received degree Jun. 1999.
- 14. Carmen Piehl (B.Sc. (project student), University of Sussex, UK). Title: "Carbon Nanotubes". Received degree Jul. 1995.
- 15. Henrik Pettersson. (B.Sc. (project student), University of Sussex, UK). Title: "Controlled Production and Characterisation of Metal nanowires". July 2001.

#### PhD Students (In progress)

 Eduardo Cruz Silva. (Ph.D. IPICYT, México). Title: "Sintesis, Caracterización y Propiedades Físicas de Nanoestructuras Dopadas". Termination July 2007.

17. José Manuel Romo Herrera (Ph.D. IPICYT, México) Title: "Jerarquía en Nanoestructuras de Carbono". Termination July 2007.

18. Leonardo Chávez Guerrero. (Ph.D. IPICYT, México). Title: "Propiedades Fisicoquímicas de los Materiales Mesoporosos". Termination July 2007.

 Marlamne deHonor Gómez. (Ph.D. IPICYT, México). Title: "Propiedades morfológicas y electrónicas de copolimeros bloque PE O-b-PS dopados con nanotubos de carbono". Termination July 2007. 20. David Meneses Rodríguez. (Ph.D. IPICYT, México). Title: "Fabricación y caracterización de una celda espintrónica". Termination July 2007.

 Abraham Cano Márquez (PhD. IPICYT, México). Title: "Modificación de nanotubos de carbono con polímeros conductores electrónicos para la síntesis y caracterización de nanocompuestos". Termination January 2010.

 Jessica Campos Delgado (PhD. IPICYT, México). Title: "Dopaje de SWNTs con distintas especies atómicas: desde síntesis y caracterización hasta su biocompatibilidad". Termination January 2010.

23. Aaron Morelos Gómez (PhD. IPICYT, México). Title: "Auto-Ensamblaje aplicado en cristales líquidos y ópalo inverso de carbono". Termination January 2010.

 Andrés Botello Méndez (PhD. IPICYT, México). Title: "Síntesis y propiedades de nuevas nanoestructuras de óxido de Zinc". Termination January 2010.

## **EXPERIMENTAL EXPERTISE**

- Arc Discharge generator for fullerene and nanotube production.
- Pyrolytic methods for aligned nanotubes production.
- Electrolytic techniques for the generation of carbon nanotubes, encapsulated materials and metal nanowires.
- X-ray diffractrometer (Siemens D-5000 CuKa).
- Transmission Electron Microscopes (JEOL 4000-EX, JEOL ARM 1250, Hitachi 7100, JEM 100CX, JEM 2000 Fx).
- Scanning Electron Microscope (Leo 5420 SEM).
- Nd:YAG Laser.
- SQUID Magnetometry (Quantum Design MPMS magnetometer).
- Conductivity Measurements (Four and two probe method, Oxford Instruments).
- Thermogravimetric Analysis (Perkin-Elmer 7 Thermogravimetric Analyzer).
- ESR measurements (Bruker ESP 300 spectrometer).

#### **COMPUTATIONAL EXPERTISE**

- Molecular Simulations using force field techniques and empirical interatomic potentials.
- Cache-Molecular Simulations.
- Data Structural Refinement (PROFIL 5.12 and REFCEL).

#### IV. HONOURS AND AWARDS

- April 2007 "Fernando Alba" Medal, awarded by UNAM (Mexico) for outstanding contributions in experimental Physics.
- Sept. 2006 "Elected TWAS Fellow." The Academy of Sciences of the Developing World for his outstanding scientific contributions in nanoscience and nanotechnology.
- Dec. 2005 "TWAS Prize in Engineering Science." Awarded by the Academy of Sciences of the Developing World for outstanding scientific contributions in the synthesis and characterization of doped nanotube structures. Brazil. Note: The youngest Scientist to receive a TWAS award ever.
- May 2005 "José Antonio Villaseñor y Sánchez" Prize for his outstanding scientific contributions in the state of San Luis Potosí. Awarded by the State of San Luis Potosí.
- Jul. 2005-Jun. 2010 National Researcher level III (Investigador del Sistema Nacional de Investigadores Nivel III). Level III is the TOP LEVEL

April 2004	Invited Profesor, Université Catholique de Louvain La Neuve & Namur University (Belgium). April-June 2004.
April 2004	Mexican Achiever Prize in Science and Technology by the Journals "Expansión" and "Vuelo" (Mexico).
March 2004	Cover Winner of the Year 2003 for the Journal Advanced Materials. The cover was published in November 2003 together with one of our papers.
Jan. 2004	Visiting Director of the International Center for Young Scientists (ICYS) at the National Institute of Materials Science (NIMS), Japan.
Dec. 2003	Member of the Evaluation for Board for Nacional Projects in Engineering CONACYT. Usually more than 500 projects per year have to reviewed and discussed for funding. (Dec. 2003 – Dec. 2006)
Nov. 2003	"El Potosí" International prize for contributions in nanoscience and Nanotechnology of Carbon. Award given to the most outstanding scientist at IPICYT.
May. 2002	"Revista DIA SIETE". Considered as the 113 Young Mexicans with present and Future.
Jun. 2002	"Revista EXPANSION". Considered as the 30 promeses in Mexico at ages between 30-40 years old. For numerous contributions in nanotechnlogy.
Oct. 2001	UNESCO, Javed Husain Prize for Young Scientists for contributions in nanotecnology of carbon and other layered materials.
Dec. 2001	Fellow of the Mexican Academy of Sciences.
Oct. 2001	Member of the Advisory Board of the International Journal CARBON (Elsevier Science, The Netherlands)
Sept. 2001	National Prize for Chemistry 2000, for contributions in Nanotechnology of layered materials.
Jun. 2000	Conference Fellowship. NATO Advanced Study Institute (ASI) award for attending: Carbon Filaments and Nnaotubes: Common Origins, Diferring Applications. Budapest, Hungary 19-30 June 2000.
Oct. 1999- Dec. 2000	Alexander von Humboldt Fellowship tenable at the Max Planck Institut für Metallforschung (Stuttgart). Research Programme entitled: "Structural and dynamic behaviour of metals encapsulated in nested fullerenes and nanotubes".
Jul. 1999- Jun. 2002	National Researcher level II (Investigador del Sistema Nacional de Investigadores Nivel II
Mar. 1999- Mar. 2001	Programa de Primas al Desempeño y Productividad del Personal Académico de la Mar. 2001 UNAM (PRIDE) Nivel C.
April 1999	Conference Fellowship "Engineering Foundation" to attend Nanocomposite Materials: Design and Applications" (Anchorage, Alaska, 28 March- 2 April, 1999)

Jan. 1999- present	Royal Society Research Fellowship at the University of Sussex. Research Programme entitled: "Novel graphite-like structures" under the supervision of H. W. Kroto (FRS).
May 1998	Conference Fellowship. NATO Advanced Study Institute (ASI) award for attending: Design and Control of Structure of Advanced Carbon Materials for Enhanced Performance. Antalya, Turkey 9th -21st May 1998.
Nov 1997- Jan. 1998	Research Fellowship sponsored by the University of California (Santa Barbara) and the Royal Society of Great Britain.
Feb. 1998	Short stay as visiting Research Fellow at the Max Planck Institut für Metallforschung/ Professor's Rühle Group (Stuttgart, Germany 22-29 February, 1998).
Jan 1997- Oct 1997	Research Fellowship at the Fullerene Science Centre (University of Sussex) sponsored by British Oxygen Company (BOC Gases)
Dec. 1996- Aug. 1995	Academic Scholarship, ORS (Overseas Research Scholarship), Committee of vice-chancellors and Principals of the Universities of the United Kingdom (Tuition and Registration fees).
Dec. 1996- Jan. 1994	Academic Scholarship, Mexican National Council for Science and Technology (full scholarship for Doctoral studies).
Jul. 1993	Fulbright Fellowship for doctoral studies by the US Government to study at Rice University, Houston (Award not taken)
Nov. 1992	The Best Student of Mexico Award, Mexican National Council for Science and Technology.
Nov. 1992	Excellent Performance Awards in Oral Thesis Defence, Universidad Iberoamericana.
Jan. 1992	Highest Grade Point Average Award, Universidad Iberoamericana.
Jan. 1992- Aug. 1987	Academic Scholarship, Secretariat of Public Education (Tuition and Registration waiver for undergraduate studies).

### **V. GRANTS AND PROJECTS**

# As Principal Investigator

Dic. 2006 \$4,000,000 (USD), awarded by CONACYT (Mexico) and the State of San Luis Potosi (Mexico). Grant entitled: "National Nanoscience and Nanotechnology Research Laboratory". Principal Investigator: Mauricio Terrones. Grant for acquiring state of the first National Nanotechnology equipment and

the establishment of the first National Laboratory in Nanoscience and Nanotechnology in Mexico.

3, .......

Nov. 2006 \$26,000 (USD), awarded by CONACYT (Mexico) and the DAAD (Germany). Grant for 2 years, entitled: "Carbon Nanotubes with metal cores: Synthesis and Electron Microscopy Experiments". Principal Investigators: Mauricio Terrones and Florian Banhart.

August. 2005 \$10,000 (USD), awarded by CONACYT (Mexico) and the University of

Texas in Austin. Grant for 1 year, entitled: "Magnetic Properties of Alloyed Nanowires inside Carbon Nanotubes: Theory and Experiment". Principal Investigators: Mauricio Terrones and Alex de Lozanne.

- June. 2005 \$31,000 (USD), awarded by CONACYT (Mexico) and the Fondo Mixto de Puebla. Grant for 2 years, entitled: "Fabricacion y caracterizacion de nanotubos de carbono dopados con fosforo y silicio". Responsible: Mauricio Terrones.
- June. 2005 \$170,000 (USD), awarded by CONACYT (Mexico) as an individual researcher project. Grant for 3 years, entitled: "Sintesis Masiva y Caracterizacion de Nanoalambres de Aleaciones Ferromagneticas para la fabricacion de nuevos Nanocompuestos Poliméricos". Responsible: Mauricio Terrones.
- Apr. 2005 \$20,000 (USD) awarded by the MIT-CONACYT consortium. Project for 2 years entitled: "Doping Single- and Double-wall Carbon Nanotubes with B or N: Experiment and Theory". Principal Investigators: Mauricio Terrones y Mildred S. Dresselhaus.
- Jan. 2005 \$130,000 (USD) awarded by CONACYT (Mexico) to the Secretariat of Health. Grant for 3 years, entitled: "NANOCIENCIA EN SALUD: PRODUCCION CONTROLADA DE NANOTUBOS DE CARBONO DOPADOS CON NITROGENO PARA LA FABRICACION DE SENSORES DE SOLVENTES CANCERIGENOS Y GASES TOXICOS". Primary Investigator: Mauricio Terrones.
- Nov. 2003 \$25,000 (USD), awarded by CONACYT (Mexico) within the PCP program, to support research of PhD. Student Benjamín Fragneud. Grant for 3 years, entitled: "Modificación de la Interface de Nanotbos de Carbono para dispersarlos en una matriz de polibutadieno". Co^applicants: Alfonso González Montiel and Jean Yves Cavllie (CNRS –Lyon, France).
- Oct. 2003 \$25,000 (USD), awarded by CONACYT (Mexico) within the PCP program, to support research of PhD. Student Mariamne DeHonor. Grant for 3 years, entitled: "Propiedades Morfológicas y Electrónicas de Copolimeros Bioque PE-Ob-PS dopados con nanotubos de carbono". Co-applicants: Alfonso González Montiel and Jean Yves Cavllie (CNRS –Lyon, France)
- Jun. 2002 \$160,000 (USD), awarded by CONACYT (Mexico) and NSF (USA) within the CIAM framework. Grant for 3 years, entitled: "Inter-American Materials Collaboration: Large scale synthesis of N-doped carbon nanotubes for the fabrication of novel polymer composites and related low dimensional materials". USA co-applicant: Prof. P.M. Ajayan.
- Jul. 2002 \$24,181.64 (USD), awarded by Universoty of California-MEXUS and CONACYT (Mexico). Grant for 2 years, entitled: "Ferromagnetic Nanowires: Controlled Production, Characterisation and Theoretical Studies". UCSB Co-applicant: Prof. Anthony K. Cheetham.
- Mar. 2002 £152,041 awarded by the EPSRC (Great Britain). Grant for 3 years, entitled: "Carbon Based Electronics: A National Consortium". Sussex Coapplicants: Prof. Harold. W. Kroto and Dr. D. R. M. Walton. This network awarded a total of ca. £2,000,000 among various universities such as Cambridge, Oxford, UCL, Liverpool, etc.
- Jan. 2002 \$130,000 (USD), awarded by CONACYT (Mexico). Grant for three years.

Poject entitled: "Controlled Production and electronic properties of novel layered nanomaterials".

Nov. 1999 \$124,979 (USD) awarded from CONACYT (Mexico). Grant for 3 years, entitled: "Produccion controlada y estudio teorico de nuevos materiales nanoestructurados". Co-aplicants: Dr. Humebrto Terrones and Dr. Jose Luis Aragon Vera.

## As Co-principal Investigator

- Apr. 2001

  Î.865,698 awarded as an European Network (Fifth Network Programme: Competitive and Sustainable Growth -Thematic Network). Grant for 4 years entitled: "Carbon Nanotubes for Future Industrial Composites: theoretical potential versus immediate applications". The network involves 13 partners from European Countries. Project responsible (Prof. Karl Schulte, Germany).
- Apr. 2001 £54,000 awarded by the EPSRC (Great Britain). Grant for 1 year (posdoctoral researcher), entitled: "Analysis and Detection of Emission during Phase Transitions -ADEPT". Co-applicant: Prof. Peter Twonsend.
- Nov. 2000 \$1,000,000 (USD) awarded by CONACYT (Mexico) and the World Bank (millennium initiative). Grant for three years (equipment, travel and subsistence), Project entitled: "Physicochemical Studies of Novel Nanostructured Materials" Co-aplicants: Dr. Jose Luis Moran-Lopez, Dr. Humebrto Terrones, Dr, Jesus Dorantes-Davila and Dr. Roberto Escudero.

# Projects with Industry and Agreements with Research Institutions

- 1. Sept. 2004. Collaboration Agreement between the National Institute of Materials Science (NIMS) and IPICYT: September 2004, Dr. M. Watanabe (NIMS) and Dr. Bando (director of ICYS) signed a Memorandum of Understanding (MOU) with IPICYT.
- 2. 2003-present. Confidential Project with Htachi Research Laboratory (Japan).
- 3. 2003 present. Confidential Project with JUMEX (Mexico). Three patents pending.
- 4. 2005 present. Confidentail Project with MABE (Mexico). Applications of Carbon Nanotubes
- 5. 2005 present. Confidential Project with CONDUMEX (Mexico). New materials in Communication Technologies.
- 7. 2005 present. Confidential Project with Peñoles (Mexico). Production of New Nanomaterials of Ag and Bi for various applications.

#### VI. OTHER ACTIVITIES

- Aug. 2005 Co-Chariman of the Symposium No. 20 (Interamerican Collaboration in Materials), held in Cancun (México) from August 21-25, 2005. As a part of the XIV International Materials Research Congress.
- April 2005 Co-Chariman of Symposium on "Science and Applications of Carbon Nanotubes" at the Maerials Research Society Spring Meeting (San

	• • •
Nov. 2004	Co-Chariman of Symposium on "Mesoscale Architectures from Nano-Units — Assembly, Fabrication, and Properties" at the Maerials Research Society Fall Meeting (Boston, MA; Nov 29 – Dec. 3, 2004).
Jul. 2004	Chariman of the 5 <sup>th</sup> International Conference on Carbon Nanotubes and Applications NANOTUBE 04, in San Luis Potosí, México (19-24 July 2004). Attended ca. 300 partciipants from 30 different countries.
May. 2004	Co-organiser of the worshop entitled "Toward s a National Initiative: Nanostructured Materials", IPICYT, México. May 2004 (sponsored by CONACYT-México).
May. 2003	Co-organiser of the worshop entitled "Toward s a National Initiative: Nanostructured Materials", IPICYT, México. May 20-22, 2003 (sponsored by CONACYT-México).
May. 2002	Co-organiser of the worshop entitled "Toward s a National Initiative: Nanostructured Materials", IPICYT, México. May 15 - 17 (sponsored by CONACYT-México).
Aug. 2001	Co-organiser of: "Nanotechnology in Carbon and Related Materials", University of Sussex, August 29 – September 1, 2001 (sponsored by the Institute of Physics, Society of Chemical Industry and the Royal Society of Chemistry).
Sept. 1999	Co-organiser of: "Nanotechnology in Carbon and Related Materials", University of Sussex, Sept. 8-10, 1999 (sponsored by the Institute of Physics, Digital Instruments, Society of Chemical Industry and the Royal Society of Chemistry).
Sept. 1998	Co-organiser of: "Nanotechnology in Carbon and Related Materials", University of Sussex, Sept. 9-11, 1998 (sponsored by the Institute of Physics, Society of Chemical Industry and the Royal Society of Chemistry).
Apr. 1998 Mar. 2000	Committee member of the British Carbon Group
Jan 1996 present	Founder and member of the Mexican Society for Crystallography
May 1995- 1999	Member of the Electrochemical Society.
May 1991- 1989	Student member of the Department of Physics Technical Committee, May Universidad Iberoamericana.
VII. ORAL PRESENTATIONS	

Francisco, CA; March 28 - April. 1, 2005).

# **VII. ORAL PRESENTATIONS**

Oct. 2005	"Nanociencia n Nanotecnología del Carbono". Invited Talk. Chemical
	Engineering Seminar. Tecnológico de Aguascalientes, Mexico (Oct. 21)

Sept. 2005 "Dopaje en Nanotubos de Carbono". Plenary Talk. XXV Confernece on Surface Science. Zacatecas, Mexico Sept. 25-30, 2005

- Sept. 2005 "Doped Nanotubes: Tpxicity and Novel Applivations". Invited Talk. Prof. Morinobu Endo, Japan (Sept. 14).

  Sept. 2005 "The importance of Doping in Nanotube Applications", invited by Dr. K.
- Hldaka Hitachi, Japan (Sept. 19).

  Sept. 2005 "Nuevos Horixontes en la Ciencia: Nanotecnología, Qué es?, Plenary talk.
- Sept. 2005 "Nuevos Horixontes en la Ciencia: Nanotecnología, Qué es?, Plenary talk. XXXIII congreso nacional de Ginecología y Obstetricia de la asociación guatemalteca de la especialidad AGOG. Guatemala, Guatemala (5-9 September, 2005)...
- Aug. 2005 "Developing Doped and Defective Nanotubes for Emerging Technologies", invited talk. Symposium No. 20 (Interamerican Collaboration in Materials), which will be held in Cancun (México) from August 21-25, 2005. As a part of the XIV International Materials Research Congress.
- June. 2005 "Nanotube Science and Technology: Present and Future", invited by Prof. Malcolm Green and the Mexican Student Society at Oxford University (Oxford University, UK).
- June. 2005 "Nuevos Horizontes en Nanociencia y Nanotecnología", invited by the Institute of Economics Research, UNAM (Mexico). Invited.
- May. 2005 "Nanotecnología", Invited by the Center of Reserach on Industrial Design UNAM (Mexico). Invited.
- Apr. 2005 "Defect Engineering: The importance of Defects in Carbon Nanostructures", invitado por el Prof. V.M. Krenke, Director of the Consortium of the Americas for Interdisciplinary Science. University of New Mexico, USA. Invited.
- Apr. 2005 "Latest Advances and Future Challenges of Nanotube Science and Technology", invitado por el Dr. Alan Hurd, director del Manuel Lujan Jr. Neutron Scattering Center, Los Alamos National Laboratory, USA. Invited.
- Apr. 2005 "Nanociencias un Campo Intrisicamente Multidisciplinar", Posgraduate Seminar at IPICYT (April, 28).
- Apr. 2005 "Nanociencias un Campo Intrisicamente Multidisciplinar". Invitado. Instituto Tecnológco de San Luis Potosí (Abril, 29).
- Mar. 2005 "Defect Nanotube Engineering: An Alternative to Novel Devices". Invited Talk. Nanocarbons Netwrok and invited by Prof. Morinobu Endo. Tokyo, Japan (March)..
- Mar. 2005 "Defect Engineering: The importance of Defects in Carbon Nanostructures", invited by por el Dr. Kishio Hidaka de la Empresa Hitachi, Japón (Marzo 25).
- Mar. 2005 "The Importance of Defects in Carbon Nanostructures: Novel Properties and Materials", invited by Prof. Yoshio Bando (director del ICYS). ICYS-NIMS, Japón (Marzo 11).

- Mar. 2005 "The Importance of Defects in Carbon materials", Invited by Prof. T. Enoki, Tokyo Institute of Technology (TIT), Tokyo, Japan (March 15).
- Feb. 2005

  "Advances and Challenges of Carbon Nanotube Science and Technology:
  The Importance of Doping". Inivted talk. Nanoscience for Advanced
  Applications: on Crossroads of Disciplines, US-Mexico Workshop
  Guanajuato, Mexico (16-19 February, 2005). Ensenada-México. Enero 17,
  2005. Invited.
- Feb. 2005 "La Nanociencia y Nanotecnología del Carbono en México: Un mito o una Realidad". VII International Symposium of Physics: Beyond the Unknown, Organizado por la Sociedad de Alumnos de Ingeniería Física Industrial (SAIFI) del ITESM (Monterrey, N.L. 17, 18, 19 February 2005) Plenary Talk.
- Jan. 2005 "El impacto de la Nanotecnología en el Desarrollo Científico y Tecnológico de México". Inivted by Dr. Arturo Serrano, Cicese, Ensenada-México. January 17, 2005. Invited.
- Dec. 2004 "Layared Nanomaterials: Curved & Doped Nanotubes, Networks and Other Forms of Carbon". Inivted by Dr. Laure Bourgois, Monash University, Australia; December 2, 2004. Invited.
- Nov. 2004 "Doped and Defective Carbon Nanostructures: Novel Functional Materials for Future Applications". Inivted Talk. 3rd International Conference on Advanced Materials Processing (ICAMP3), Melbourne, Australia, Nov. 29 Dec. 1. Invited.
- Nov. 2004 "Layared Nanomaterials: Doped Nanotubes, Networks and Other Forms of Carbon". Inivted by Professor Gordon Wallace, Wolgonging University, Australia; November 13, 2004. Invited.
- Nov. 2004 "Building Novel Functional Nano-Materials: Doped and Defective Carbon Nanotubes". Inivted Talk. 2<sup>nd</sup> Nanocarbons Meeting; Nagano November 15 18, 2004. Invited.
- Nov. 2004 "La importancia del Dopaje en Aplicaciones de los nanotubos de Carbono". Invited. Congreso Internacional en Ciencia e Ingeniería de Materiales, Querérataro, México; Nov. 8 -12, 2004.
- Oct. 2004 "La Historia de la Nanotecnología y sus Alcances". Invited during a workshop on Science Press, Week os Science and Technology in Mexico; Oct. 25 29, 2004, Monterrey, Mexico. Invited.
- Oct. 2004 "Nanotecnología en el IPICYT". Invited during the Week os Science and Technology in Mexico; Oct. 25 29, 2004, Monterrey, Mexico. Invited.
- Sept. 2004 "Advances and Challenges of Heteroatomic Nanotube Science and Technology". Invited Plenary Talk. During the 2nd Mexican Meeting on Mathematical and Experimental Physics; El Colegio Nacional Sep. 6 10, 2004. Plenary Talk.
- Oct. 2004 "New Directions in Carbon Nanotube Science: Controlled Synthesis, Electronic Properties and Novel Devices using B- and N-doped systems: nanotubes, doping, applications". Inivted Talk, III Meeting of the Brazilian

Society for Materials Research, October 10 - 13, 2004; Foz de Iguaçu, Brazil. Invited.

- Oct. 2004 "New Directions of Carbon Nanotube Science: Importance of Defects and Doping". Plenary Talk. Nanotec 2004, Batz-sur-Mer, France Oct. 10-15, 2004. Plenary.
- July 2004 "Nanociencia y Nanotecnología del Carbono: Teoría, Síntesis, Caracterización y Aplicaciones ". Invited by Prof. Miguel Angel Vidal; ICO, Universidad Autonoma de San Luis Potosi, San Luis Potosí, México. Invited.
- June 2004 "Perspectives of Science in Mexico". Invited by the Association of Mexican Students at Cambridge University, UK.
- June 2004 "Carbon Related Nanomaterials: Controlled Synthesis, Electronic Properties and Novel Devices". Invited by Dr. Andrea Ferrari and Prof. W.I. Milne. Cambridge University, UK. Invited.
- Mayo 2004 "Layered Nanomaterials: Doped Nanotubes, Networks and Other Forms of Carbon". Invited Talk, Physics Department, Namur University (Mayo 25 Mayo 26, 2004). Invited.
- Mayo 2004 "Defect Engineering and the Role of Defects: The Formation of Novel Carbon Structures with Novel Properties". Invited talk during the Belgian Physical Society Meeting, Mons, Belgium (25-26 de Mayo, 2004). Invited.
- Mayo 2004 "Latest Advances and Future Challenges of Carbon Nanotube Science and Technology". Plenary Talk during the XXVII Encontro Nacional de Física da Materia Condensada, Poços de Caldas, Brasil (May 4 8, 2004).
- Abril 2004 "Advances and Challenges of Carbon Nanotube Science and Technology". Invited talk during the worshop entitled "Frontiers of Materials Research: A CIAM, CIMAT CONICYT WORKSHOP, Viña del Mar, Chile (Abril 25 Abril 29, 2004). Invited
- Mar. 2004 "Novel Carbon Nanotube Composites: 2D Networks and SiOx-tube Materials". Nanocarbons Worshop, invited by Prof. Morinobu Endo; Tokyo, Japan.
- Mar. 2004 "Polymerization and Fusion of Carbon Nanopepods: A Route to Novel One-dimensional Materials", Invited talk within the Conference Particles 2004, Orlando, Florida (USA); March 6-10, 2004.
- Mar. 2004 "Advanced Layered Nanomaterials: Doped Nanotubes, Networks and Other Forms of Novel Carbon", invited by Prof. Yoshio Bando (director Of ICYS). ICYS-NIMS, Japan.
- Mar. 2004 "Doped Carbon Nanotubes as new components of Nanotechnology Devices", invited by Dr. Kishio Hidaka; Hitachi, Japan.
- Feb. 2004 "Creation of Novel Composites with Carbon Nanotubes: Recent Advances and Challenges", invited by Prof. Morinobu Endo. Shinshu University, Japan.
- Feb. 2004 "Doped Nanotubes, 2D networks and Other Novel Forms of Nano-sacle

Carbon", invited by Prof. Riichiro Saito. Tohoku University, Japan:

- Feb. 2004 "Doped Nanotubes, 2D Networks and Other Novel Forms of Nano-sacle Carbon", invited by Prof. Sumio lijima & Dr. Masako Yudasaka NEC, Japan.
- Nov. 2003 "Nanciencia y Nanotecnolgiía en México: Síntesis y Caracterización de Nuevas Estructuras". Presented in the National Meeting of Crystallography (Morella, Michoacán). (Plenary Talk).
- Nov. 2003 "Jueguemos con Atomos y moléculas y Hagamos Nuevos Materiales".

  Presented in the Secretariat of Education of the State of Coahuila (Saltillo, Coahuila) under the 10<sup>th</sup> week of Science and Technology. (Invited Talk, 2 November).
- Oct. 2003 "Síntesis de Nanoestructuras Laminares y sus Aplicaciones". Peresented in the Chemistry Seminar, Universidad Autónoma de San Luis Potosí. (Invited Talk, 7 October).
- Sept. 2003 "Materiales Avanzados". Presented in the Secretariat of Education of the State of Puebla (Puebla, Puebla) under the First Meeting on Nanoscience and Nanotechnology. (Invited Talk, 25 September).
- Sept. 2003 "La Nanociencia del Carbono: teoría, Síntesis y Caracterización". Presented in Center for Physics, UNAM (Cuernavaca, Morelos) the Science Museum, México City (UNIVERSUM). (Invited Talk, 24 September).
- Sept. 2003 "Juguemos con Atomos y Hagamos Nuevos Materiales: Desarrollo de la Nanotecnología". Presented in the Science Museum, México City (UNIVERSUM). (Invited Talk, 23 September).
- Aug. 2003 "Synthesis of Novel Layered Nanostructures and the Creation of 2D and 3D Carbon Nanotube Networks". Presented in The II Applied Statistical Physics: Molecular Engineering Conference (ASTATPHYS-MEX-2003). (Invited Talk).
- Aug. 2003 "Advanced Nanomaterials: Doped Nanotubes, Networks and Other Novel Forms of Carbon". Presented at the Max- Planck Institut für Metalforschung (Stuttgart, Germany, 22 August 2003). (Invited Scientist).
- Aug. 2003 "Building the Carbon Nanocosmos". Present at the Center for Solid State Science Arizona State University, USA. (15 August, 2003). (Invited Talk).
- Aug. 2003 "In-situ welding of Single-walled carbon nanotubes and melting of encapsulated metal clusters". Presented at the Microscopy and Microanalysis Meeting, San Antonio, TX –USA (3-7 August). (Invited Speaker).
- Jul. 2003 "Materiales Laminados". Presented at the Material Science Course for Posgraduate Students. Universidad de Concepción (Chile). (Invited Lecturer).
- Jul. 2003 "Layered Nanomaterials: Controlled Synthesis, Theoretical Studies and Applications". Presented at The International Conference on the Science and Application of Nanotubes NANOTUBE 03. Held in Seoul Korea (7-11 July 2003). (Invited Speaker).

- Jun. 2003 "Building Carbon Nanodevices". Presented the Symposium of Modern Physisc in Honour of Sir Roger Elliot, Instituto de Física UNAM (México, DF; 17-19 Jun 2003). (Invited Talk).
- Jun. 2003 "Layered Nanomaterials: Controlled Synthesis, Theoretical Studies and Electronic Properties". Presented in the Pan American Advanced Study Institute on Physics at the Nanometer Scale (Bariloche, Argentina, 8-18 June 2003). (Invited Speaker).
- May 2003 "Exploring the Carbon Nanocosmos: Doped Nanotubes, Networks and Other Forms of Carbon". Presented at the SPIE meeting on Microelectrnics for the new Millennium 2003 (Maspalomas, Canary Islands, 19-21 May 2003). (Keynote Lecture).
- May 2003 "Building Novel Carbon Nanostructures in the Electron Microscope". Presented in the Second Mexican workshop on Nanoscience and Nanotechnology (15-17 May, 2003), held at IPICYT (México). (Invited Talk).
- May 2003 "Novel Carbon-Carbon Nanocomposites: Building 2D and 3D single-walled nanotube networks". Presented in the Electrochemical Society Meeting, Paris (May 2003). (Invited Talk).
- Nov. 2002 "Nanotecnología del Carbono y sus Aplicaciones en el Siglo XXI". Presented at the XXIV Congreso Internacional de Metalurgia y Materiales. Instituto Tecnológico de Saltillo.(November 8th, 2002) (Invited Talk).
- Nov. 2002 "Nuevas Nanoestructuras Laminadas: Producción Controlada, Caracterización y Nuevas Tecnologías" Presented at the XXXIV Congreso de Ingeniería y Ciencia de Materiales, Tecnológico de Querétaro (November 7th, 2002) Querétaro, Qro., Mexico. (Invited Talk).
- Oct. 2002 "Nuevas Nanoestructuras Laminadas: Produción Controlada, Caracterización y Nuevas Tecnologías", Presented at the Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León (October 24th, 2002). (Invited Talk).
- Oct. 2002 "Nanotecnología del Carbono". Presented at the Engineering Institute, UNAM, Mexico City. (October 14th, 2002) (Invited Talk).
- Sept. 2002 "Nanotecnología en América Latina: un mito o una realidad". Presented at the Segunda Semana de las Ingenierías, Universidad Iberoamericana, Mexico City. (September 30th, 2002). (Inaugural conference).
- Sept 2002 "Novel Advances in the Synthesis and Applications of Doped Carbon Nanotubes" Presented at Hitachi Company (24 September 2003).
- Sept 2002 "Connecting Carbon Nanotubes" Presented at the Second International Workshop on Quantum Nonplanar Nanostructures and Nanoelectronics 02" (8 –11 September 2003).
- Sept. 2002 "Novel Carbon-Carbon Nanotube Composites: 2D and 3D Tube Networks". Presented in Carbon 2002, Beijing (15-20 September, 2002).
- Aug. 2002 "La nanotecnología del Carbono". Presented at IPICYT, San Luis Potosí, S : L. P. (Invited Talk).

- Aug. 2002 "Towards nano-device fabrication: joining and connecting single-walled carbon nanotubes". Presented in Nanotec 02, University of Sussex, UK. (28-31 August, 2002). Invited Talk.
   Jul. 2002 "Boron-, Nitrogen- and Iron-doped Carbon Nanomaterials: Controlled Synthesis, Electronic Properties and Novel Molecular Devices". Presented in Nanotube 02, Boston, USA. (6-11 July 2002). Invited Talk.
- Jun. 2002 "Nanotubes: Synthesis and Electronic Properties". Presented at Shinshu University, Japón. (June 2002). Invited Talk.
- May. 2002 "Synthesis of Novel Layered Nanostructures and the Creation of 2D and 3D Carbon Nanotube Networks". Peresented at the Institute of Materials, CSIC-Barcelona, Spain. Invited Talk.
- April. 2002 "Layered Nanomaterials: Controlled Synthesis, Theoretical Studies and Electronic Properties". Presented at the Rensselaer Polytechnic Institute, USA. Invited Talk.
- Feb. 2002 "Making Carbon Nanotube Junctions: Fabrication and Electronic Properties". Presented in Shinshu University, Nagano, Japan. Invited Talk.
- Feb. 2002 "Exploring the Carbon Nanocosmos: Doped Nanotubes, Networks and Other Novel Forms of Carbon". Presented in University of Louvain La Nueve, Belgium. Invited Talk.
- Feb. 2002 "Carbon Related Nanomaterials: Controlled Synthesis, Electronic Properties and Novel Devices". Presented at the Materials Department, University of Leeds, UK. Invited Talk.
- Feb. 2002 "Novel Carbon Nanotube Composites: Networks and SO<sub>x</sub>-tube materials". Presented at the CNT European Network meeting, Lyon France (27 Febraury 1 March). Inivited Talk.
- Nov. 2001 "Explorando el Nanocosmos: Producción y Aplicaciones de Nanotubos de Carbono". Presented at the First Anniversary of IPICYT. San Luis Potosí, México (24 November 2001). Plenary Talk.
- Nov. 2001 Nanoestructuras de Carbono: Síntesis Controlada, Propiedades Fisicoquímicas y Aplicaciones". Presented at the weekly seminar series of the Chemistry Department. Universidad Autónoma de San Luis Potosí. San Luis Potosí, México (28 November 2001). Inivited Talk.
- Nov. 2001 "Novel doped and undoped Nanocarbons: The development of emerging technologies". To be presented at Nanocarbons, Nagano, Japón (Nov. 11-16, 2001) Invited.
- Sep. 2001 "Carbon related nanomaterials: Controlled synthesis, electronic properties and applications". To be presented at NANOCOMP-workshop: "Nanotubes: Production, Characterization and Application". Zaragoza España (10 September 2001). Invited.
- Jul. 2001 "Novel layered nanomaterials: Controlled synthesis, electronic properties and applications". To be presented at International Workshop on the Science and Application of Nanotubes, Potsdam, Germany (July 22-25, 2001) Invited.

Jul. 2001	"Connecting and Joining Carbon Nanotubes". To be presented at the American Carbon Society CARBON 2001 Conference. Lexington, Kentucky USA (July 14-19, 2001).
Mar. 2001	"Advances on the growth and properties of n and b-doped carbon nanotubes". Presented at Euroconference on Electronic Properties of Novel Materials:, Kirchberg / Tirol Austria International Winterschool on Electronic Properties of Novel Materials IWEPNM 2001 (3-10 March, 2001). Invited.
Nov. 2000	"Electronic Properties of Carbon Nanotubes". Presented at Sinshu University, Nagano, Japón. Invited.
Sep. 2000	"Controlled Synthesis of Carbon Nanostrcutures" (invited). Presented at Nanotubes and Nanostructures 2000, Sardegna, Italy (24-30 Sept. 2000).
July 2000	"Efficient Routes to Large Arrays of $CN_x$ Nanofibres". Presented at EUROCARBON 2000, Berlin, Germany (9-13 July 2000).
June 2000	"Controlled Synthesis of Tubular Carbon and $B_xC_yN_z$ Architectures" (invited). Presented at the Advanced Study Institute (ASI): Carbon Filaments and Nnaotubes: Common Origins, Diferring Applications. Budapest, Hungary 19-30 June 2000.
June 2000	"Controlled Fabrications of $\text{CN}_x$ Nanostroutures" (invited). Presented at TRANSDIAM, Amiens, France (5-8 June 2000).
May 2000	"Structure, Synthesis and Applications of Novel Carbon Nanostructures" (invited). Presented at EPSRC meeting for Carbon Based Electronics (London, May 31).
May 2000	"Defects in Carbon Nanotubes" (invited). Presented at the Indian Institute of Science, Bangalore, India.
May 2000	"Synthesis and properties of dichalcogenide Nanotubes" (invited). Presented at General Electric India Technology Centre, Bangalore, India.
Jan. 2000	"New Metallic Allotropes of Carbon". (invited) Presented at the National Institute for Research in Inorganic Materials (NIRIM), Tsukuba, Japan
Jan. 2000	"Novel advances in the creation of Nanostructures". (invited) Presented at the National Institute of Materials and Chemical Research (NIMC), Tsukuba, Japan
Jan. 2000	"Novel Advances in the Creation of Metal-filled Nanotubes". (inivited). Presented in Shinshu University, Nagano, Japan.
March 1999	"Self Assembly generation of Novel Nanocomposites". Presented in: Nanocomposite Materials: Design and Applications (Anchorage, Alaska, 28 March- 2 April, 1999). Invited speaker.
Feb. 1999	"Novel Advances in the Creation of layered C <sub>x</sub> N <sub>y</sub> and B <sub>x</sub> C <sub>y</sub> N <sub>z</sub> Nanostructures by Self Assembly Processes". Presented at the Materials Research Laboratory, University of California at Santa Barbara, USA. Invited speaker.

- Sept. 1998 "BN, BCN and CN nanotubes with interesting morphologies". Presented in: "Nanotechnology in Carbon and Related Materials", University of Sussex, Sept. 9-11, 1998.
- Sept. 1998 "Aligned Carbon Nanotubes". Presented at the 14th. International Congress on Electron Microscopy (Cancún, México, 31 Aug- 4 Sept. 1998).
- Aug. 1998 "Production of Aligned Doped Carbon Nanotubes and Metal Nanowires".
  Presented at the International Meeting on Materials Science; Synthesis and Applications of Fullerene and Nanotubes (Cancún, México, 30 Aug.-4 Sept. 1998). Invited speaker.
- Apr. 1998 "Carbon self assembly: Formation of Aligned Nanotubes". Presented at the British Carbon Conference, University of Bath-UK, 15-16 April 1998). Invited speaker.
- Mar. 1998 "Nanotechnology of Nanotubes and Nanowires: From Carbon Nanotubes to Silicon Oxide Nanowires". Presented at Euroconference on Molecular Nanostructures:, Kirchberg / Tirol Austria International Winterschool on Electronic Properties of Novel Materials IWEPNM 98 (1-7 March, 1998). Invited speaker.
- Feb. 1998 "Novel routes to Nanotubes and Nanowires". Presented at the Max Planck Institut für Metallforschung (Stuttgart, Germany 23 February). Invited speaker.
- Jan. 1998 "Nanotechnology of Nanowires and Nanotubes". Presented at the XII Latin American Conference in Solid State Physics (Oaxaca, Mexico, 11-16 January 1998). Invited speaker.
- Dec. 1997 "Fullerenes and Nanotubes". Presented at the Defence Evaluation Research Agency (DERA-Malvern; Electronic Materials and Characterisation). Invited speaker (Malvern, UK, 3 December 1997).
- Sept. 1997 "Advances in the creation of Novel Nanoscale Materials". Presented at the 3rd Human Capital and Mobility (HCM) Workshop on "Formation, Stability and Photophysics of Fullerenes" (Brugge, Belgium, 17-21 September 1997).
- May 1997 "Production of Novel B<sub>x</sub>C<sub>y</sub>N<sub>z</sub> Nanomaterials and Metal Nanowires". Presented at the Electrochemical Societty 191st. meeting (Montreal-Quebec, May 4-9, Canada).
- Jan. 1997 "Fullerenes: A New Form of Carbon". Presented at Universidad Iberoamericana, Mexico City, México.
- Jan. 1997 "Fullerenes: A New Form of Carbon". Presented at the Sotero Prieto Seminar Series, Instituto de Física, UNAM-MEXICO (México)
- Dec. 1996 "Production and Characterisation of Novel Fullerene-related Nanostructures: Nanofibres, Nanowires and Nanotubes". Presented at the Physics Department, Universidad Autónoma de San Luis Potosí, San Luis Potosí, México.
- March 1996 \* "Morphology effects of catalytic particles in pyrolytic grown B<sub>x</sub>C<sub>y</sub>N<sub>z</sub> nanofibres and nanotubes". Presented at the Euroconference on Fullerenes and Fullerene Nanostructures, Kirchberg / Tirol Austria

International Winterschool on Electronic Properties of Novel Materials IWEPNM 96.

\* "Production of carbon nanotubes and graphitic onions by condensed phase electrolysis". Presented at the Euroconference on Fullerenes and Fullerene Nanostructures, Kirchberg / Tirol Austria International Winterschool on Electronic Properties of Novel Materials IWEPNM 96.

- Jan. 1996 "New graphitic structures and their physico-chemical implications". Presented at the Sotero Prieto Seminar Series, Instituto de Física, UNAM-MEXICO
- Nov. 1995 "New graphitic structures and their physico-chemical implications". Presented at the Chemical Physics Seminar, University of Sussex.
- May 1995 "Physico-chemical studies on Nanotubes and their encapsulated compounds". Presented at The Electrochemical Society 187th. Meeting (Reno, Nevada, USA).

  \* Vice-chairman in the Nano-encapsulates session.
- March 1995 "New observations on Carbon Nanotubes". Presented at The Southern Spectroscopy group Meeting, University of Bristol.
- Apr. 1992 "Asymptotic Analysis of a Model Integro-Differential Equation that Exhibits Travelling Wave Solutions". Presented at the Leopoldo García-Colin Seminar Series Universidad Iberoamericana.

### VIII. POSTERS AND OTHER PRESENTATIONS

- Jul. 2000 Coating of Carbon Nanotubes. Seeger, T., Kohler-Redlich, Ph., Grobert, N., Terrones, M., Walton, D. R. M., Kroto, H. W., Rühle, M. EUROCARBON 2000, Vol. 2, 1033-1034, Berlin, Germany, 9-13/07/2000.
- Jul. 2000

  A novel route to Iron-filled Nanowires, Grobert, N., Terrones, H., Hsu, W.K., Zhu, Y. Q., Walton, D. R. M., Kroto, H. W., Terrones, M., Han, W. Q., Kohler-Redlich, Ph., Seeger, T., Ruehle, M., Morales, F., Escudero, R. EUROCARBON 2000, Vol. 2, 1033-1034, Berlin, Germany, 9-13/07/2000.
- Nov. 1999 *Metal chalcogenide nanotubes: structure and electronic properties*, <u>Seifert</u>, <u>G.</u>, Jungnickel, G., Frauenheim, T., Terrones, H. and Terrones, M. Proceeding of ISCAN meeting (USA, nov. 1999. Poster).
- Sept. 1999 On the structure and electronic structure of MoS<sub>2</sub> nanotubes, <u>Seifert, G.,</u> Jungnickel, G., Terrones, H., Terrones, M. and Freuenheim, Th., NanoteC99, Brighton, England (8-10 september 1999, Talk).
- Sept. 1999 Self assembly generation of Si-based nanostructures. Zhu, Y.Q., Hu, W.B., Hsu, W.K., Terrones, H., Terrones, M., Grobert, N., Hare, J.P., Kroto, H.W. and Walton, D.R.M., NanoteC99, Brighton, England (8-10 September 1999. Talk)
- Sept. 1999 New Metallic Allotropes of Planar and Tubular Carbon: Haeckelites.

  Terrones H., Terrones, M., Hernández, E., Grobert, N., Charlier, J.C.C.
  and Ajayan, P.M.A, NanoteC99, Brighton, England (8-10 september 1999, Talk).
- Ago. 1999 A New Form of Crystalline Layered Carbon: Characterisation, Stability and

Electronic Properties. <u>Terrones, M.</u>, Charlier, J-C, Grobert, N., Ajayan, P.M. and Terrones, H., XVIII Congress of the International Union of Crystallography, (Glasgow, Scotland, 4-13 august 1999. Poster).

- Abr. 1999 Atomic self-assemble generation of aligned carbon nanotube films and silica nanowires. Terrones, M., Grobert, N., Zhu, Y.Q., Hsu, W.K., Trasobares, S., Hare, J.P., Kroto, H.W., Walton, D.R.M., and Terrones, H. Nanocomposite Materials Design and Applications, (Anchorage, Alaska USA) 03/04/1999.
- Abr. 1999 In-situ filling of carbon nanotubes: generation of ferromagnetic nanowires.

  Grobert, N., Terrones, M., Zhu, Y.Q., Hsu, W.K., Trasobares, S., Hare,
  J.P., Walton, D.R.M., Kroto, H.W. and Terrones, H. Nanocomposite
  Materials Design and Applications, (Anchorage, Alaska USA) 03/04/1999.
- Sep. 1999

  New Metallic Allotropes of Planar and Tubular Carbon: Haeckelites.

  Terrones H., Terrones, M., Hernández, E., Grobert, N., Charlier, J.C.C. and Ajayan, P.M. NanoteC99 (Brighton, England) 09/09/1999.
- Sep. 1999 Self assembly generation of Si-based nanostructures. Zhu, Y.Q., Hu, W.B., Hsu, W.K., Terrones, H., Terrones, M., Grobert, N., Hare, J.P., Kroto, H.W. and Walton, D.R.M. NanoteC99 (Brighton, England) 08/09/1999.
- Sep. 1999 On the structure and electronic structure of MoS₂ nanotubes. Seifert, G., Jungnickel, G., Terrones, H., Terrones, M. and Freuenheim, Th. NanoteC99 (Brighton, England) 09/09/1999.
- Nov. 1999 Metal chalcogenide nanotubes: structure and electronic properties. Seifert, G., Jungnickel, G., Frauenheim, T., Terrones, H. and Terrones, M. Proceeding of ISCAN meeting (USA) 10/11/1999.
- Sep. 1998 "Recent advances in the synthesis and characterizations of B-doped carbon nanotubes", Ph. Redlich, W.K. Hsu and M. Terrones. Presented in the workshop entitled: Simulation of carbon and composite B<sub>x</sub>C<sub>y</sub>N<sub>z</sub> nanotubes. CECAM, Lyon, France 1-3 September, 1998
- Sep. 1998 "Metal-Catalysed growth of carbon nanotubes", D. J. Wallis, N. Grobert, C. L. Reeves, A. J. Pidduck, D. R. M. Walton, J. P. Hare, W. K. Hsu, M. Terrones, H. W. Kroto, P. J. Wright, C. Vizard. Poster presented at the 14th. International Congress on Electron Microscopy Cancún, México, August 31- September 4 1998.
- Aug. 1998 "Electrolytic Formation of Metal Nanowires", W. K. Hsu, M. Terrones, H. Terrones, N. Grobert, Y. Q. Zhu, J. P. Hare, H. W. Kroto, D. R. M. Walton. Poster presented at the 14th. International Congress on Electron Microscopy (Cancún, México, 31 Aug- 4 Sept. 1998).
- May. 1998 "Controlled Production of Aligned Carbon Nanotubes". M. Terrones. Poster presented at the Advanced Study Institute (AIS) in design and control of structure of advanced carbon materials for enhanced performance. Antalya, Turkey 9th -21st May 1998.
- Apr. 1998 "Geometry and Energetics of High Genus Fullerenes and Nanotubes", H. Terrones & M. Terrones. Workshop on Discrete Mathematical Chemistry at the Centre for Discrete Mathematics and Theoretical Computer Science (DIMACS), Rutgers University NJ, USA, 23-25 March 1998.

- Aug. 1997 "Radio-Thermoluminiscence Spectra of Fullerenes", A. P. Rowlands, M. Terrones, P. D. Townsend, K. Kordatos. Electrochemical Society Meeting, Paris, France, August 31- September 5 1997. In Luminescent materials VI.,
- June 1997 "Fullerenes and Nanotubes with Non-Positive Gaussian Curvature", H. <u>Terrones</u> and M. Terrones. International Conference on Advanced Materials (ICAM 97), Symposium A: Fullerenes and Carbon Based Materials, Strasbourg, France, (16-20 June 1997).
- May 1997 "Structure and Electronic Properties of High Genus Fullerenes with Non-positive Gaussian Curvature", H. Terrones, J. L. Ricardo-Chávez, J. Dorantes-Dávila, M. Terrones. 191st. Electrochemical Society Meeting, Montreal, Canada, May 4-9, 1997.
- May 1997 "LDF Calculations on Large Fullerenes and Onions", M.I. Heggie, M. Terrones, B. R. Eggen, H. Terrones, G. Jungnickel, R. Jones, P. R. Briddon. 191st. Electrochemical Society Meeting, Montreal, Canada, May 4-9, 1997.
- March 1997 "Controlled Production of Nanotubes via Pyrolytic Techniques", M. Terrones, N. Grobert, J. Olivares, K. Kordatos, W.K. Hsu, J. P. Zhang, H. Terrones, J. P. Hare, P. D. Townsend, K. Prassides, A. K. Cheetham, H. W. Kroto, D. R. M. Walton. Presented at the Euroconference on Fullerenes and Fullerenes related Materials, Kirchberg / Tirol Austria International Winterschool on Electronic Properties of Novel Materials IWEPNM 97.
- March 1997 "Production and Characterisation of Metal Nanowires by Condensed-Phase Electrolysis", W. K. Hsu, M. Terrones, H. Terrones, J. P. Hare, N. Grobert, A. I. Kirkland, H. W. Kroto, D. R. M. Walton. Presented at the Euroconference on Fullerenes and Fullerenes related Materials, Kirchberg / Tirol Austria International Winterschool on Electronic Properties of Novel Materials IWEPNM 97.
- Dec. 1996 "Quasicrystalline Graphite Sheets and High Genus Fullerenes with Non-Positive Gaussian Curvature", <u>H.Terrones</u> and M. Terrones, Symposium D, 1996 MRS (Materials Research Society) Fall Meeting, Boston, MA, December 2-6 1996.
- Oct. 1996

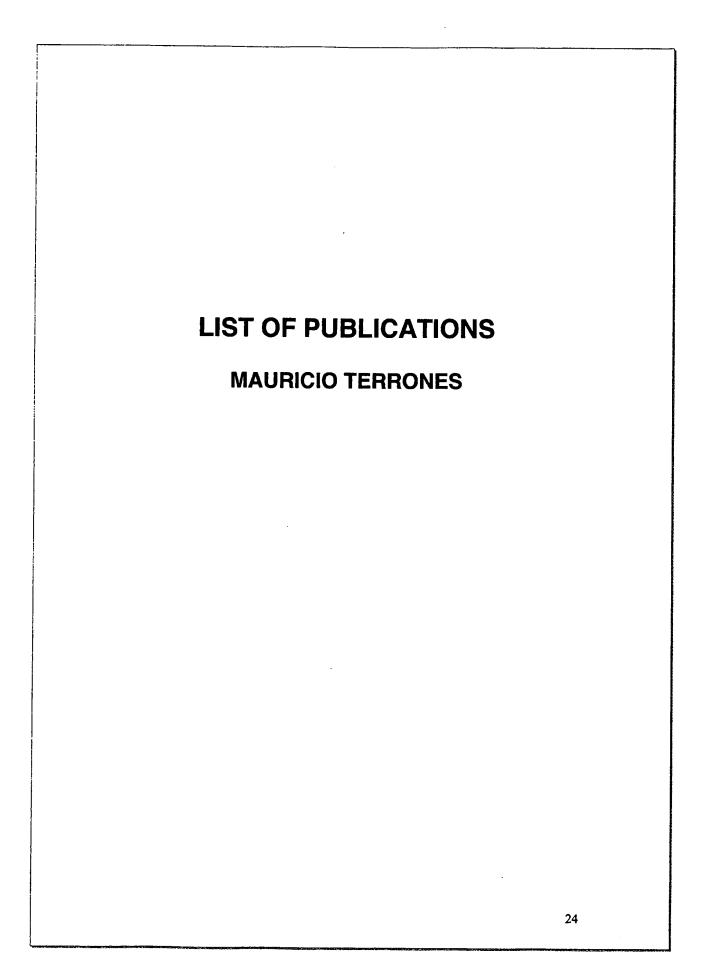
  "Know your onions!; Reliable Calculations in Materials Science" Heggie, M.
  L. Eggen, B. R., Terrones, M., Jungnickel, G., Latham, C. D., Jones,
  R., Briddon, P. R., Terrones, H. Consortium e6; Ab Initio Simulations of
  Covelent Materials, EPSRC High Performance Computing Initiative, Town
  Meeting, U.K.
- Sept. 1996 "LDF calculations on large fullerenes and onions" Heggie, M. I., Eggen B. R., Terrones, M., Jungnickel, G., Latham, C. D., Jones, R., Briddon, P. R. Network Conference; Ab initio calculations of complex processes in materials. Schwäbisch Gmünd, Germany.
- August 1996 "Geometry and Stability of Graphitic Onion-Like Structures", H. Terrones and M. Terrones, International Union of Crystallography XVII Congress and General Assembly, Seattle, WA, USA, august 8-17 1996.
- July 1996 "The Role of Defects in Fullerene-related Structures" Terrones, H., Terrones, M., Fullerenes 96, Oxford, U. K.
- Dec. 1995 "Growth Mechanism for Graphitic Onions" Terrones, H and Terrones, M.

Materials Research Society (MRS) Fall Meeting. Boston, MA, USA

Sept 1995 "The Role of Boron Nitride in the Production of Long Graphite Nanotubes" Terrones, H., García-Cruz R., Castillo R., Ramos, S., Terrones, M., Hsu, W. K., Prassides, K., Walton, D. R. M., Kroto, H. W. IV International Conference on Advanced. Cancún, México.

Sept. 1995 "Symmetry and Energy Studies on Defective Graphitic Particles: A new approach to explain bucky-onion growth" Terrones, H and Terrones, M. IV International Conference on Advanced Materials. Cancún, México.

June 1995 "Fullerene based Materials Science at Sussex". Hare, J. P., Hsu, W. K., Terrones, M., Sarkar, A., Firth, S. G., Lappas, A., Abeysinghe, J. R., Kroto, H. W., Prassides, K., Taylor, R. and Walton D. R. M. 1995. St. Petersburg Conference.



#### **PUBLICATIONS**

#### **Books**

Terrones, M. & Terrones, H. (Eds) "Nanotechnology of Carbon and Related Materials" Philosophical Transactions, The Royal Society (UK), October 2004.

#### **Patents**

Title: Mesoporous Boron Nitride Materials and Their Preparation Methods Inventors: Ajayan Vinu, Katsuhiko Ariga, Mauricio Terrones, Dimitri Golberg, Toshiyuki Morl. Application number: 2005-212474 (Japanese patent).

## C) Articles in refereed journals and contributions to books

- 1) Rodríguez-Manzo, J.A., Terrones, M., Terrones, H., Kroto, H.W., Sun, L., Banhart, F. (2007) "In-situ nucleation of carbon nanotubes by the injection of carbon atoms into metal particles". Nature Nanotechnology 2, 307-311.
- Romo-Herrera, J.M., Terrones, M., Terrones, H., Dag, S., Meunier, V. (2007). "Covalent 2D and 3D 2) Networks from 1D Nanostructures: Designing New Materials". Nano Letters 7, 570-576.
- 3) Rodríguez-Manzo, J. A., Lopez-Urias, F., Terrones, M., Terrones, H. (2007) "Anomalous Paramagnetism in Doped Carbon Nanostructures". Small 3, 120-125.
- Terrones H. & Terrones, M. "The Shape of Carbon Novel Materials for the 21st Century". In WSPC
- Advanced in Nanoengineering. Ed. G. Davies. World Scientific. Singapore 2007, in press. Muramatsu, H, Hayashi, T, Kim Y.A., <u>Terrones, M</u>, Endo, M. (2006). "Formation of off-centered doublewalled carbon nanotubes exhibiting wide interlayer spacing from bi-cables". Cheimical Physics Letters 432, 240-244.
- Ayala, P., Freire, F. L., Gu, L., Smith, D. J., Solorzano, I.G., Macedo, D.W., Vander Sande, J.B., Terrones, H., Rodríguez-Manzo, J., <u>Terrones, M.</u> (2006) "Decorating carbon nanotubes with nanostructured nickel particles via chemical methods". *Cheimical Physics Letters* **431**: 104-109.
- Lopez-Urias, F., Rodríguez-Manzo, J. A., Muñoz-Sandoval, E., Terrones, M., Terrones, H. (2006) 7) "Magnetic response in finite carbon graphene sheets and nanotubes". Optical Materials 29: 110-115.
- Kim, Y.A., Muramatsu, H., Hayashi, T., Endo, M. Terrones, M., Dresselhaus, M.S. (2006). "Fabrication of high-purity, double-walled carbon nanotube buckypaper". Chemical Vapor Deposition 12: 327-330.
- Endo, M., Takeuchi, K., Tajirir, T., Park, K.C., Wang, F., Klm, Y.A., Hayashi, T., <u>Terrones, M.</u>, Dresselhaus, M.S. (2006). "Sodium chloride-catalyzed oxidation of multiwalled carbon nanotubes for environmental benefit". Journal of Physical Chemistry B 110, 12017-12021.
- 10) Sun, L., Banhanrt, F., Kraheninnikov, A.V., Rodríguez-Manzo, J.A., Terrones, M., Ajayan, P.M. (2006). "Carbon Nanotubes as High Pressure Cylinders and Nanoestruders". Science 312, 1199-1202.
- 11) Endo, M., Kim, Y.A., Hayashi, T., Muramatsu, H., Terrones, M., Saito, R., Villalpando-Paez, F., Chuo, S. G., Dresselhaus, M.S. (2006). "Nanotube Coalescence-Inducing Mode: A Novel Vibrational Mode in Carbon Systems". Small 2, in press.
- 12) Fantini, C., Cruz, E., Jorio, A., Terrones, M., Terrones, H., Van Ller, G., Charlier, J.-C., Dresselhaus, M. S., Saito, R., Kim, Y.A., Hayashi, T., Muramatsu, H., Endo, M., Pimenta, M.A, (2006). "Resonante Raman Study of linear chains fromed by the heat treatment of double-wall carbon nanotubes". Pysical Review B (Brief Reports) 73, in press.
- Carrero-Sánchez, J.L., Elías, A.L., Mancilla, R., Arellín, G., Terrones, H., Laclette, J.P., Terrones, M. (2006). "Biocompatibility and Toxicological Studies of Carbon Nanotubes doped with Nitrogen". Nano Letters, in press.
- Villalpando-Paez, F., Zamudio, A., Elias, A.L., Son, H., Barros, E.B., Chou, S. G., Kim, Y.A., Muramatsu, H., Hayashi, T., Kong, J., Terrones, H., Dresselhaus, G., Endo, M., <u>Terrones, M.</u>, Dresselhaus, M.S. (2006). "Synthesis and characterization of long strands of nitrgen-doped singles-walled carbon nanotubes". Chemical Physics Letters, in press.
- 15) Castañeda, L., Garcia-Valenzuela, A., Zironi, E.P., Canetas-Ortega, J., Terrones, M., Maldonado, A. (2006). "Formation of indium-doped zinc oxide thin films using chemical spray techniques: The importance of acetic acid content in the aerosol solution and the substrate temperature for enhancing electrical transport". Thins Solid Films 503, 212-218.
- 16) Kim, Y.A., Muramatsu, H., Hayashi, T., Endo, M., Terrones, M., Dresselhaus, M.S. (2006) 'The possible way to Evaluate the Purity of Double Walled Carbon Nanotubes over Single Wall Carbon Nanotubes by Chemical Doping". Chemical Physics Letters 420 (4-6): 377-381.
- 17) Terrones, H., López-Urías, F., Muñoz-Sandoval, E., Rodríguez-Manzo, J.A., Zamudio, A., Elías, A.L. and <u>Terrones</u>, M. (2005). "Magnetism in Fe-based and Carbon Nanostructures: Theory and Applications". Solid State Sciences 8 303-320.
- 18) Muramatsu, H., Hayashi, T., Kim, Y.A., Shimamoto, D., Kim, Y.J., Tantrakam, K., Endo, M., Terrones, M., <u>Dresselhaus, M.S.</u> (2005) "Pore structure and oxidation stability of double-walled carbon nanotube-derived bucky paper". *Chemical Physics Letters* 414, 444-448
- Kim, Y.A., Kojima, M., Muramatsu, H., Umemoto, S., Watanabe, T., Yoshida, K., Sato, K., Ikeda, T., Hayashi, T., Endo, M., Terrones, M., Dresselhaus, M.S. (2005) "In-situ Raman study on single- and double-walled carbon nanotubes as a function of Lithium Insertion". Small 2, 667-676
- Zamudio, A., Elías, A.L. Rodríguez-Manzo, J.A., López-Urias, F., Rodríguez-Gattorno, G., Lupo, F.,

Rühle, M., Smith, D.J., Terrones, H., Díaz, D. and <u>Terrones, M.</u> (2005) "Efficient Anchoring of Silver Nanoparticles on N-doped Carbon Nanotubes". *Small* 2, 346-350.

 Fragneaud, B., Masenelli-Varlot, K., González-Montiel A., <u>Terrones, M.</u>, Cavalllé, J.-Y. (2005). "Efficient coating of N-doped carbon nanotubes with polystayrene using atomic transfer radical polymerization". *Chemical Physics Letters* 419, 567-573.

 Muñoz-Navia, M., Dorantes-Dávila, J., <u>Terrones, M.</u>, Terrones, H. (2005). "Ground-state electronic structure of nanoscale carbon cones". *Physical Review B* 72, 235403.

 Dehonor, M., Masenelli-Varlot, K., González-Montiel, A., Gauthier, C., Cavaillé, J.Y., Terrones, H and Terrones, M.. (2005). "Nanotube Brushes: Polystyrene grafted covalently on CN<sub>x</sub> Nanotubes by nitroxidemediated radical polymerization" Chemical Communications 5349-5351.

24) Vinu, A., <u>Terrones, M.</u>, Golberg, D., Mori, T., Arlga, K. (2005). "Synthesis of Nanoporous BN and BCN exhibiting Large Surface Areas via Templating Methods". Chemistry of Materials Chemistry of Materials 17, 5887-5890.

 J. J. Velázquez-Salazar, E. Muñoz-Sandoval, J. M. Romo-Herrera, F. Lupo, M. Rühle, H. Terrones and M. Terrones. (2005). Chemical Physics Letters 416, 342-348.

Terrones, M. (2005). "Controlling Nanotube Chirality and Crystallinity by Doping". Small 1, 1032-1034
 Banhart, F., Li, J., <u>Terrones, M.</u> (2005) "Cutting Single-Walled Carbon Nanotubes with an Electron Beam: Evidence for Atom Migration Inside Nanotubes". Small 1, 953-956.

28) López-Urías, F., Muñoz-Sandoval, E., Reyes-Reyes, M., Romero, A.H., <u>Terrones, M.</u>, Morán-López, J.L. (2005). "Creation of helical vortices during magnetization of aligned carbon nanotubes filled with Fe: Theory and experiment". *Physical Review Letters* 94, 216102.

29) Muñoz-Navia, M., Dorantes-Dávila, J., Terrones M., Havashi, T., Kim, Y.A., Endo, M., Dresselhaus, M.S., Terrones, H. (2005). "Synthesis and electronic properties of coalesced graphitic nanocones". Chemical Physics Letters 407, 327-332.

Romero, A.H., García, M.E., Valencia, F., Terrones, H., Terrones, M., Jeschke, H.O.(2005)
 "Femtosecond Laser Nanosurgery of Defects in Carbon Nanotubes". Nano Letters 5, 1361-1365.

31) Endo, M., Muramatsu, H., Hayashi, T., Kim, Y.A., Van Lier, G., Charlier, J.-C., Terrones, H., <u>Terrones, M.</u>, Dresselhaus, M. (2005). "Atomic Nanotube Welders: Boron Interstitials Triggering Connections in Double-Walled Carbon Nanotubes". *Nano Letters* 5, 1099,1105.

32) Lupo, F., Rodriguez-Manzo, J.A., Zamudio, A., Elias, A.L., Kim, Y.A., Hayashi, T., Muramatsu, H., Kamalakaran, R., Terrones, H., Endo, M., Rühle, M., <u>Terrones, M.</u> (2005). "Pyrolytic synthesis of long strands of large diameter single-walled carbon nanotubes at atmospheric pressure in the absence of sulphur and hydrogen". *Chemical Physics Letters* 410, 384-390.

33) Rodíguez-Manzo, J.A., López-Urías, F., <u>Terrones, M.</u>, Terrones, H. (2005) "Ring currents in Carbon Naostructures: Magnetic Field Effects". In Statistical Physics and Beyond: 2<sup>rd</sup> Mexican Meeting on Mathematical And Experimental Physics. Editors: F.J. Uribe, L. García-Colin S. and E. Díaz-Herrera. American Institute of Physics (USA).

34) Webster, S., Reyes-Reyes, M., Pedron, X., López-Sandoval, R., <u>Terrones, M.</u>, Carroll, D.L. (2005). "Enhanced Nonlinear Transmittance by Complementary Nonlinear Mechanisms: a reverse saturable absorbing dye blended with nonlinear scattering carbon nanotubes". *Advanced Materials* 17, 1243-1248.

35) Muramatsu, H., Hayashi, T., Kim, Y.A., Endo, M., <u>Terrones, M.</u>, Dresselhaus, M.S. (2005) "Growth of double-walled carbon nanotubes using a conditioning catalyst". *Journal of Nanoscience and Nanotechnology* 5, 404-408.

36) Terrés, E., Panella, B., Hayashi, T., Kim, Y.A., Endo, M., Dominguez, J.M., Hirscher, M., Terrones, H., <u>Terrones, M.</u> (2005). "Hydrogen Storage in Nanoporous Carbon". Chemical Physics Letters 403, 363-366

Elías, A.L., Rodríguez-Manzo, J.A., McCartney, M.R., Golberg, D., Zamudio, A., Baltazar, S.E., López-Urías, F., Muñoz-Sandoval, E., Gu, L., Tang, C.C., Smith, D.J., Bando, Y., Terrones, H., <u>Terrones, M.</u> (2005). "Production and Characterization of Single-Crystal FeCo Nanowires Inside Carbon Nanotubes" Nano Letters, 5, 467-472.

 Endo, Y.A., Muramatsu, H., Kim, Y.A., Hayashi, T., <u>Terrones, M.</u>, Dresselhaus, M. (2005) "Buckypaper of Coaxial Nanotubes". *Nature* 433, 476.

39) Endo, Y.A., Hayashi, T., Kim, Y.A., <u>Terrones, M.</u>, Dresselhaus, M. (2004) History and Latest Advances in carbon nanotube science and technology. Chimica Oggi (Chemistry Today), October 2004, 13-19.

 Rodíguez-Manzo, J.A., López-Urías, F., <u>Terrones, M.</u>, Terrones, H. (2004) "Magnetism in corrugated carbon nanotori: The importance of symmetry, defects, and negative curvature". Nano Letters 4, 2179-2183.

41) Kim, Y.A., Muramatsu, H., Hayashi, T., Endo, M., <u>Terrones, M.</u>, Dresselhaus, M. (2004) "Thermal stability and structural changes of double-walled carbon nanotubes by heat treatment". Chemical Physics Letters 398, 87-92.

 Endo, M., Hayashi, T., Kim, Y.A., <u>Terrones, M.</u>, Dresselhaus, M. (2004) "Applications of Carbon Nanotubes in the XXI Century". *Philosophical Transactions A, The Royal Society* 362, 2223-2238.

43) <u>Terrones, M.</u> (2004) "Carbon nanotubes: synthesis and properties, electronic devices and other emrging applications". *International Materials Reviews* 49, 325-377.

44) Terrones, H., Terrones, M., López-Urías, F., Rodríguez-Mazo, J.A., Mackay, A.L. (2004) "Shape and Complexity at the atomic scale: Tha case of layered materials" *Philosophical Transactions A, The Royal Society* 362, 2039-2063.

45) Reyes-Reyes, M., Grobert, N., Kamalakaran, R., Seeger, T., Golberg, D., Rühle, M., Bando, Y., Terrones, H., <u>Terrones, M.</u> (2004) "Efficient encapsulation of gaseous nitrogen inside carbon nanotubes with bamboo-like structure using aerosol thermolysis". Chemical Physics Letters 396, 167-173.

- 46) Doytcheva, M., Kaiser, M., Reyes-Reyes M., Terrones, M., de Jonge, N. (2004) "Electron emission from
- individual nitrogen-doped multi-walled carbon nanotubes". Chemical Physics Letters 396, 126-130.

  Terrones, M., Jorio, A., Endo, M., Rao, A.M., Kim, Y.A., Hayashi, T., Terrones, H., Charlier, J.C., Dresselhaus, G., Dresselhaus, M.S. (2004) "New Directions of Nanotube Science: Properties, Characterization and Applications of B- and N-doped systems". Materials Today Magazine 7, 30-45.
- Page, K., Proffen, T., Terrones, H., <u>Terrones, M.</u>, Lee, L., Yang, Y., Stemmer, S., Seshadri, R., Cheetham, A.K. (2004) "Direct observation of the structure of gold nanoparticles by total scattering powder neutron diffraction". Chemical Physics Letters 393, 385-388.
- Endo, M., Hayashi, T, Muramatsu, H., Kim, Y.A., Terrones, H., Terrones, M., Dresselhaus, M.S. (2004). "Coalescenec of Double-walled Crabon Nanotubes: Formation of Novel Bicables". Nano Letters 4, 1451-
- Rocquefelte, X. Rignanese, G.-M., Meunier, V., Terrones, H., Terrones, M., Charlier, J.-C. (2004) "How 50) to Identify Haeckelite Sructures: A Theoretical Study of their Electronic and Vibrationla Properties". Nano Letters, 4, 805-810.
- Yoon, M., Seungwu, H., Kim, G., Lee S.B., Beber, S., Osawa, E., Ihm, J., Terrones, M., Banhart, F., Charlier, J.-C., Grobert, N., Terrones, H., Ajayan, P.M., Tomanek, D. (2004) "Zipper Mechanism of Nanotube Fusion: Theory and Experiment". *Physical Review Letters* 92, art. No. 075504.
- Banhart, F., Hernandez, E., Terrones, M. (2004) Comment on "Extreme superheating and supercooling of encapsulated metals in fullerenelike shells" - Reply. Physical Review Letters 92, art. no. 139602.
- Villalpando-Paéz, F., Romero, A., Muñoz-Sandoval, E., Martínez, L.M., Terrones, H., Terrones, M. (2004) "Fabrication of Vapor and gas sensores using films of aligned Cox nanotubes". Chemical Physics Letters 386, 137-143.
- Jiang, K.Y., Schadler, L.S., Siegel, R.W., Zhang, X.J., Zhang, H.F., Terrones, M. (2004) "Protein immobilization on carbon nanotubes via a two-step process of diimide-activated amidation" Journal of Materials Chemistry 14, 37-39.
- López-Urías, F., Terrones, Mr., Terrones, H. (2003) "Electronic properties of giant fullerenes and complex graphitic nanostrutures with novel morphologies". Chemical Physics Letters 381, 683-690.
- Charlier, J.-C., Terrones, M., Bahart, F., Grobert, N., Terrones, H., Ajayan, P.M. (2003) "Experimental Observation and Quantum Modeling of Electron Irradiation on Single wall carbon nanotubes" IEEE Transactions on Nanotechnology 2, 349-354.
- Terrones, M., Golberg, D., Grobert, N., Seeger, T., Reyes-Reyes, M., Mayne, M., Kamalakaran, R., Dorozhkin, P., Dong, Z.C., Terrones, H., Rühle, M., Bando, Y. (2003) "Production and state-of-the-art characterization of aligned nanotubes with homogeneous BC<sub>x</sub>N (1  $\leq$  x  $\leq$  5) compositions". Advanced Materials, 15, 1899-1905.
- Terrones, M. & Terrones, H. (2003) "The carbon nanocosmos: novel materials for the XXI century". Trienial Issue of Philosophical Transactions A, The Royal Society. 361, 2789-2806.
- 59) Terrones, H & Terrones, M., (2000) "The shape of graphitic structures". In Fullerenes (Ed. P. M. Ajayan, Y. Rubin). Vol. 2; Carbon series (Series editor P. Delhaes), Gordon & Breach, in press.
- Hernández, E. Meunier, V., Smith, B.W., Rurali, R., Terrones, H., Buongiorno Nardelli, M., Terrones. M., Luzzi, D.E., Charlier, J.-C. (2003) "Fullerene Coalescence in Nanopeapods: A Path to Novel Tubular Carbon". Nano Letters 3, 1037-1042.
- 61) Endo, M., Lee, B.J, Kim, Y.A., Kim, Y.J., Muramatsu, H., Yanagisawa, T., Hayashi, T., Terrones, M., Dresselhaus, M.S. (2003) "Transitional behaviour in the transformation from active end planes to stable loops caused by annealing" New Journal of Physics 5, art. no. 121.1-121.9.
- Valencia, F., Romero, A., Hemández, E., Terrones, M., Terrones, H. 'Theoretical characterisation of 62) several models of nanoporous carbon". New Journal of Physics 5, art. no. 123.1-123.16.
- 63) Terrones H., Terrones M. (2003). "Curvarure in Nanomaterials". New Journal of Physics 5, art. no. 126.1-126.37
- Endo, M., Kim, Y.A., Hayashi, T., Yanagisawa, T., Muramatsu, H., Ezaka, M., Terrones, H., Terrones, M., Dresselhaus, M.S. (2003) "Microstructural changes induced in "stacked cup" carbon nanofibers by heat treatment". Carbon 41, 1941-1947.
- Endo, M., Kim, Y. A., Ezaka, M., Osada, K., Yanagisawa, T., Hayashi, T., <u>Terrones, M.</u>, Dresselhaus, M.S. (2003). "Selective and Efficient Impregnation of Metal Nanoparticles on Cup-Stacked-Type 65) Carbon Nanofibers". Nano Letters 3, 723 - 726.
- Choi, Y.M., Lee, D.S., Czerw, R., Chiu, P.W., Grobert, N., <u>Terrones, M.</u>, Reyes-Reyes, M., Terrones, H., Charlier, J.-C., Ajayan, P.M., Roth, S., Carroll, D.L., Park, Y.W. (2003). "Nonlinear Behavior in the 66) Thermopower of Doped Carbon Nanotubes Due to Strong, Localized States" Nano Letters 3, 839 -
- 67) Terrones, M., Charlier, J.C., Banhart, H., Grobert, N., Ajayan, P.M. (2002) "Towards Nanodevice Fabrication: Joining and Connecting Single-walled Carbon Nanotubes". New Dianond & Frontier Carbon Technology 12, 315-323
- Golberg, D., Bando, Y., Mitome, M., Kurashima, K., Sato, T., Grobert, N., Reyes-Reyes, Terrones, H., Terrones, M. (2002). "Preparation of aligned BN and B/C/N nanotubular arrays and their characterization using HRTEM, EELS and energy-filtering TEM". Physica B - Condensed Matter 323. 60-66.
- Terrones, M. (2003) "Science and Technology of the XXI Century: Synthesis, Properties and 69) Applications of Carbon Nanotubes". Annual Reviews of Materials Research 33, 419-501.
- Banhart, F., Hernandez, E., Terrones, M. (2003) "Extreme superheating and supercooling of encapsulated metals in fullerenelike shells" Physical Review Letters 90, art. no. 185502.

- 71) Jiang, K.Y., Eitan, A., Schadler, L.S., Ajayan, P.M., Siegel, R.W., Grobert, N., Mayne, M., Reyes-Reyes, M., Terrones, H., <u>Terrones, M.</u> (2003). "Selective attachment of gold nanoparticles to nitrogen-doped carbon nanotubes" *Nano Letters* 3, 275-277.
- 72) Golberg, D., Dorozhkin, P.S., Bando, Y., Dong, Z.C., Grobert, N., Reyes-Reyes, M., Terrones, H., <u>Terrones, M.</u> (2003). "Cables of BN-insulated B-C-N nanotubes" *Applied Physics Letters* 82, 1275-1277.
- 73) Golberg, D., Dorozhkin, P.S., Bando, Y., Dong, Z.C., Tang, C.C., Uemura, Y., Grobert, N., Reyes-Reyes, M., Terrones, H., <u>Terrones, M.</u> (2003) "Structure, transport and field-emission properties of compound nanotubes: CNx vs. BNCx (x < 0.1)" *Applied Physics A Materials Science & Processing* 76, 499-507.
- 74) Rühle M, Seeger T, Redlich P, Grobert N, <u>Terrones M</u>, Walton DRM, Kroto HW. (2002). "Novel SiOx-coated carbon nanotubes" *JOURNAL OF CERAMIC PROCESSING RESEARCH* 3, 1-5.
- 75) Charlier, J.C., <u>Terrones, M.</u>, Baxendale, M., Meunier, V., Zacharia, T., Rupesinghe, N.L., Hsu, W.K., Grobert, N., Terrones, H., Amaratunga, G.A.J. (2002). "Enhanced electron field emission in B-doped carbon nanotubes". *Nano Letters* 2, 1191-1195.
- 76) Terrones, H., Hayashi, T., Murioz-Navia, M., <u>Terrones, M.</u>, Kim, Y. A., Grobert, N., Kamalakaran, R., Dorantes-Dávila, J., Escudero, R., Dresselhaus, M. S. (2002). "Graphitic cones in carbon nanofibres", *Molecular Crystals and Liquid Crystals* 387, 263-274.
- 77) <u>Terrones, M.</u>, Ajayan, P.M., Banhart, F., Blase, X., Carrol, D.L., Charlier, J.C., Czerw, R., Foley, B., Grobert, N., Kamalakaran, R., Kohler-Redlich, Ph., Rhule, M., Seeger, T., Terrones, H. (2001) "Doping and Connecting Carbon Nanotubes", *Molecular Crystals and Liquid Crystals*, 387, 275-286.
- 78) Marco, J.F., Gancedo, J.R.s, Hernando, A., Crespo, P., Prados, C., Gonzalez, J.M., Grobert, N., <u>Terrones, M.</u>, Walton, D.R.M., Kroto, H.W. (2002) "Mossbauer study of iron-containing carbon nanotubes". *Hyperfine Interactions* 139, 535-542.
- 79) Seeger, T., Kohler, T., Frauenheim, T., Grobert, N., <u>Terrones, M.</u>, Seifert, G., Ruhle, M. (2002). "SiO2-coated carbon nanotubes: theory and experiment". *Zeitschrift Für Metallkunde* 93, 455-458.
- 80) Ajayan, P.M., Ramanth, G., <u>Terrones, M.</u>, Ebbesen, T.W. (2002). "Igniting nanotubes with a Flash Reponse". Science 297, 192-193.
- 81) Golberg, D., Bando, Y., Mitome, M., Kurashima, K., Grobert, N., Reyes-Reyes, Terrones, H., <u>Terrones. M.</u> (2002) "Nanocomposites: Synthesis and Elemental mapping of aligned B-C-N nanotubes". Chemical Physics Letters 360, 1-7.
- 82) <u>Terrones, M.,</u> Grobert, N., Terrones, H., (2002) "Synthetic routes to Nanoscale B<sub>z</sub>C<sub>y</sub>N<sub>z</sub> architectures", Carbon 40, 1665, 1684.
- 83) Terrones, M., Terrones, G., Terrones, H. (2002) "Structure, Chirality, and Formation of Giant Icosahedral Fullerenes and Spherical Graphitic Onions". Structural Chemistry 13, 373-384.
- 84) <u>Terrones, M., Banhart, H., Grobert, N., Chartier, J.C., Ajayan, P.M. (2002) "Molecular Junctions by joining Single-walled Carbon Nanotubes"</u>. *Phys. Rev. Lett.* 89, 075505-1-075505-4.
- 85) Coleman, K.S., Sloan, J., Hanson, N.A., Brown, G., Clancy, G.P., <u>Terrones, M.</u>, Terrones, H., Green, M.L.H. (2002). "The formation of ReS2 inorganic fullerene-like structures containing Re-4 parallelogram units and metal-metal bonds". *Journal of the American Chemical Society (JACS)* 124, 11580-11581.
- 86) Golberg, D., Bando, Y., Mitome, M., Kurashima, K., Grobert, N., Reyes-Reyes, M., Terrones, H., Terrones, M. (2002). "Nanocomposites: synthesis and elemental mapping of aligned B-C-N nanotubes". Chemical Physics Letters 360, 1-7.
- 87) Hayashi, T., <u>Terrones, M.</u>, Scheu, C., Kim, Y.A., Ruhle, M., Nakajima, T., Endo, M. (2002). "Nanoteflons: Structure and EELS Characterization of Fluorinated Carbon Nanotubes and Nanofibres". Nanotetters 2, 491-496.
- 88) Ajayan, P.M., <u>Terrones, M.</u>, de la Gaurdia, A., Huc, V., Grobert, N., Wei, B.Q. Lezec, H., Ramanath, G., Ebbesen, T.W. (2002). "Nanotubes in a Flash: Ignition and Reconstruction". Science 296, 705 (2002).
- 89) <u>Terrones, M.</u>, Ajayan, P.M., Banhart, F., Blase, X., Carrol, D.L., Chariler, J.C., Czerw,R., Foley, B., Grobert, N., Kamalakaran, R., Kohler-Redlich, P., Ruhle, M., Seeger, T., Terrones, H. (2002) "N-doping and Coalescence of Carbon Nanotubes: Synthesis and Electronic Properties", *Applied Physics A* 74, 355-361.
- 90) Golberg, D., Bando, Y., Sato, T., Grobert, N., Reyes-Reyes, M., Terrones, H., <u>Terrones, M.</u> (2002) "BN nanocages: super-high pressure nanocells for encapsulation of solid Nitrogen". *Journal of Chemical Physics* 116, 8523-8532.
- 91) Prados, C., Crespo, P., Gonzalez, J.M., Hernando, A., Marco, J.F., Gancedo, R., Grobert, N., <u>Terrones, M.</u> Walton, D.R.M., Kroto, H.W. (2002) 'Hysteresis shift in Fe-filled carbon nanotubes due to gamma-Fe'. *Physiscal Review B* 65, 113405.
- 92) Endo, M., Kim, Y.A., Hayashi, T., Fukai, Y., Oshida K., <u>Terrones, M.</u>, Yanagisawa, T., Higaki, S., Dresselhaus, M.S. (2002). "Structural characterization of cup-stacked-type nanofibers with an entirely hollow core". *Applied Physics Letters* 80, 1267-1269.
- 93) Sloan, J., <u>Terrones, M.</u>, Nufer, S., Friedrichs, S., Ruehle, M., Green, M.L.H. (2002). "Metastable one-dimensional AgCl<sub>1-kh</sub> solid-solution wurzite 'tunnel' crystals formed within single walled carbon nanotubes". *Journal of the American Chemical Society (JACS)* 124, 2116-2117.
- 94) Terrones, M & Terrones, H. (1999) "Structure and Formation of Fullerenes". In The Encyclopedia of Materials: Science and Technology; Ed. P. A. Thrower (Pergamon, Elsevier Science ISBN 0-08-0431526) pp-3372-3379.

- 95) Seeger, T., Köhler, Th. Frauenheim, Th., Grobert, N., Rühle, M., Terrones, M., Seifert, G. (2002) "Nanotube Composites: Novel SiO₂ Coated Carbon Nanotubes". Chemical Communications 35, 34-35.
- 96) Banhart, F., Grobert, N., Terrones, M., Charlier, J.C., Ajayan, P.M. (2001). "Metal atoms in carbon nanotubes and related nanoparticles". International Journal of Modern Physics B 15, 4037-4069.
- Zhu, Y.Q., Hsu, W.K., Zhou, W.Z., Terrones, M., Kroto, H.W., Walton, D.R.M. (2001). "Selective Co-97) catalysed growth of novel MgO fishbone fractal nanostructures" . Chemical Physics Letters 347, 337-
- 98) Terrones, H., Terrones, M., Moran-Lopez, J.L. (2001) "Curved nanomaterials". Current Science 81, 1011-1029
- Prados, C., Crespo, P., Gonzalez, J.M., Hernando, A., Marco, J.F., Gancedo, R., Grobert, N., Terrones, M., Walton, D.R.M., Kroto, H.W. (2001) "Magnetic and hysteretic properties of Fe-filled 991 nanotubes" IEEE Transactions on Magnetics 37, 2117-2119.
- 100) Zhu Y.Q., Hsu W.K., Firth, S., Terrones M., Clark R.J.H., Kroto H.W., Walton D.R.M. (2001) "No-doped WS2 nanotubes", Chemical Physics Letters 342, 15-21.
- Endo, M., Kim, Y.A., Fukai, Y., Hayashi, T., Terrones, M., Terrones, H., Dresselhaus, M.S. (2001). "Comparison study of semi-crystalline and highly crystalline multiwalled carbon nanotubes". Applied Physics Letters 79, 1531-1533.
- 102) Czerw, R., Terrones, M., Charlier, J.C., Blase, X., Foley, B., Kamalakaran, R., Grobert, N., Terrones, H., Tekleab, D., Ajayan, P.M., Blau, W., Rühle, M., Carroll, D.L. (2001). "Identification of Electron Donor States in N-Doped Carbon Nanotubes" Nanoletters 1, 457-460.
- Hsu, W.K., Zhu, Y.Q., Firth, S., Terrones, M., Terrones, H., Trasobares, S., Clark, R.J.H., Kroto, H.W., Walton, D.R.M. (2001). "WxMoyCzS2 nanotubes", Carbon 39, 1107-1111.
- Terrones, H., Hayashi, T., Muñoz-Navia, M., Terrones, M., Kim. Y.A., Grobert, N., Kamalakaran, R., 104) Dorantes-Dávila. J., Escudero, R., Dresselhaus, M.S., Endo, M. (2001) "Graphitic cones in palladium catalysed carbon nanofibres", Chemical Physics Letters 343, 241-250.
- Seeger, T., Redlich, Ph., Grobert N., Terrones, M., Walton, D.R.M., Kroto, H.W., Rühle, M. (2001). 'SiO<sub>x</sub>-Coating of Carbon Nanotubes at Room Temperature", Chemical Physics Letters 339, 41-46.
- 106) Mayne, M. Grobert, N., Terrones, M., Kamalakaran, Rühle, M., Walton, D. R. M., Kroto, H. W., Walton, D. R. M., (2001) "Pyrolytic production of aligned carbon nanotubes from homogenously dispersed benzene-based aerosols", Chemical Physics Letters 338, 101-107.
- Terrones, M. (2001). "Controlled Synthesis of Tubular Carbon and B,C,Nz Architectures", In Carbon Filaments and Nanotubes: Common Origins, Differing Applications?, NATO Science Series, Eds. L. Biro, C. A. Bernardo, G. G. Tibbetts and Ph. Lambin (Kluwer Academic Publishers, Boston USA), pp. 171-186.
- 108) Grobert, N., Mayne, M. Terrones, M., Sloan, J., Dunin-Borkowski, R. E., Kamalakaran, R., Seeger, T., Terrones, H., Rühle, M., Walton, D. R. M., Kroto, H. W., Hutchison, J. L. (2001) "Alloy Nanowires: Invar inside carbon nanotubes", Chemical Communications 5, 471-472.
- Zhu Y.Q., Hsu W.K., Terrones M., Firth S., Grobert N., Clark R.J.H., Kroto H.W., Walton D.R.M. (2001)
- "Tungsten-niobium-sulfur composite nanotubes", Chemical Communications 1, 121-122.
  Hsu W.K., Zhu Y.Q., Boothroyd C.B., Kinloch I., Trasobares S., Terrones H., Grobert N., Terrones M., Escudero R., Chen G.Z., Colliex C., Windle A.H., Fray D.J., Kroto H.W., Walton D.R.M. (2000) "Mixedphase W<sub>x</sub>Mo<sub>y</sub>C<sub>z</sub>S<sub>2</sub> nanotubes", Chemistry of Materials 12, 3541-3544.
- 111) Hsu, W. K., Zhu, Y Q., Kroto, H. W., Walton, D. R. M., Kamalakaran, R., Terrones, M. (2000) "C-MoS2 and C-WS₂ Nanocomposites", Applied Physics Letters 77, 4130-4132.
- Terrones, M. Hayashi, T. Nishimura, K., Endo, M. Terrones, H. Hsu, W. K., Grobert, N., Zhu, Y. Q., Kroto, H. W., Walton, D. R. M. (2000). "Carbon Nanotubes and Nanofibres: Exotic Materials of Carbon", TANSO 145, 424-433.
- 113) Terrones, M., Kamalakaran., Seeger, T., Rühle, M. (2000) "Novel nanoscale gas containers: encapsulation of N₂ in CNx nanotubes", Chemical Communications 23, 2335-2336.
- Zhu, Y Q., Hsu, W. K., Terrones, H., Grobert, N., Chang, B. H., Terrones, M., Wei, B.Q., Kroto, H. W. Walton, D. R. M., Boothroyd, C. B., Kinloch, I., Chen, G. Z., Windle, A. H., Fray, D. J. (2000) "Morphology, structure and growth of WS2 nanotubes", Journal of Materials Chemistry 10, 2570-2577.
- Hsu, W. K., Chang, B.H., Zhu, Y Q., Han, W. Q., Terrones, H., Terrones, M., Grobert, N., Cheetham, A.K., Kroto, H. W., Walton, D. R. M. (2000) "An Alternative route to Molydenum Disulphide Nanotubes", Journal of the American Chemical Society 122, 10155-10158.
- Kamalakaran, R., <u>Terrones, M.</u>, Seeger, T., Kohler-Redlich, Ph., Rühle, M., Kim, Y. A. Hayashi, T., Endo, M. (2000) "Synthesis of Thick and Crystalline Nanotube Arrays by Spray Pyrolysis", *Applied* Physics Letters 77, 3385-3387.
- 117) Selfert, G., Terrones, H., Terrones, M., Frauenheim, T. (2000). "Novel Mettalic NbS₂ nanotubes", Solid State Communications 115, 635-638.
- Grobert, N., Hare, J. P., Hsu, W.K., Kroto, H. W., Terrones, M., Walton, D. R. M., Zhu, Y. Q. (2000) "New advances in the creation of nanostructures materials", Pure and Applied Chemistry 71, 2125-2130.
- 119) Han, W.Q. Kohler-Redlich, P., Seeger, T., Ernst F., Rühle, M., Grobert, N., Hsu, W. K., Zhu, Y. Q., Terrones, M., Terrones, H., Kroto, H. W. Walton, D. R. M. (2000). "Aligned N-doped Nanotubes by pyrolysis of ferrocene/C<sub>60</sub> under NH₃ atmosphere", Applied Physics Letters 77, 1807-1809.
- Han, W.Q. Kohler-Redlich, P., Scheu, C., Ernst F., Rünle, M., Grobert, N., Terrones, M., Kroto, H. W. 120) Walton, D. R. M. (2000). "Carbon nanotubes as nanoreactors for boriding iron nanowires", Advanced Materials 12, 1356-1359.

- 121) Rowlands, A. P., Karali, T., <u>Terrones, M.</u>, Grobert, N., Townsend, P.D., Kordatos, K. (2000). "Cathodoluminescence of fullerene C<sub>60</sub>", Journal of Physics: Condensed Matter 12, 7869-7878.
- 122) Selfert, G., Terrones, H., <u>Terrones, M.</u>, Jungnickel, G., Frauenheim, T. (2000). "Structure and electronic properties of MoS₂ nanotubes", *Physical Review Letters* 85, 146.
- 123) <u>Terrones, M., Terrones, H., Charlier, J.C., Banhart, F., Ajayan, P.M. (2000). "Coalescence of Single walled Carbon Nanotubes", Science 288</u>, 1226-1229.
- 124) Seifert, G., Terrones, H., <u>Terrones, M.</u>, Jungnickel, G., Frauenheim, T. (2000). "On the Electronic Structure of WS₂ nanotubes", *Solid State Communications* 114, 245-248.
- 125) Hsu, W.K., Chu, S.Y., Murioz-Picone, E., Boldú, J.L., Firth, S., Franchi, P., Roberts, B.P., Schilder, A., Terrones, H., Grobert, N., Zhu, Y.Q., Terrones, M., McHenry, M.E., Kroto, H.W., Walton, D.R.M. (2000) "Metallic behaviour of boron-containing carbon nanotubes" Chemical Physics Letters 323, 572-579.
- 126) Zhu, Y.Q., Hsu, W.K., Grobert, G., Chang, B.H., <u>Terrones, M.</u>, Terrones, H., Kroto, H.W., Walton, D.R.M. Wei, B. Q. (2000) "In-situ production of WS₂ nanotubes" *Chemistry of Materials* 12, 1190-1194.
- 127) Zhu, Y.Q., Hsu, W.K., Grobert, G., Terrones, M., Terrones, H., Kroto, H.W., Walton, D.R.M. Wei, B. Q. (2000) "Self assembly of Si-Nanostroutures" Chemical Physics Letters 322, 312-320.
- 128) Hsu, W.K., Firth, S., Redlich, P., Terrones, M., Terrones, H., Zhu, Y. Q. Grobert, G., Schilder, A. Clark, R. J. H., Kroto, H. W., Walton, D. R. M. (2000) "Boron doping effects in carbon nanotubes", Journal of Materials Chemistry 10, 1425-1429.
- 129) Terrones, H., <u>Terrones, M.</u>, Hernández, E., Grobert, N., Charlier, J.C., Ajayan, P.M. (2000) "New metallic allotropes of planar and tubular carbon", *Physical Review Letters* 84, 1716.
- Hu, W.B., Zhu, Y.Q., Hsu, W.K., Chang, B.H., <u>Terrones, M.</u>, Grobert, N., Terrones, H., Hare, J.P., Kroto, H.W., Walton, D.R.M. (2000), "Generation of Hollow Crystalline Tungsten Oxide Fibres". Applied Physics A 70, 231-233 (rapid communication).
- 131) Grobert, N., <u>Terrones, M.</u>, Trasobares, S., Kordatos, K., Terrones, H., Olivares, J., Zhang, J.P., Redlich, Ph., Hsu, W.K., Reeves, C.L., Wallis, D.J., Zhu, Y.Q., Hare, J.P., Pidduck, A.J., Kroto, H.W., Walton, D.R.M. (2000), "A Novel Route to Aligned Nanotubes and Nanofibres using Laser Patterned Catalytic Substrates". *Applied Physics A* 70 175-183.
- Hsu, W.K., Li, W.Z., Zhu, Y.Q., Grobert, N., Terrones, M., Terrones, H., Yao, N., Zhang, J.P., Firth,S., Clark, R.J.H., Cheetham, A.K., Hare, J.P., Kroto, H.W. and Walton, D.R.M. (2000). "KCl crystallization within the space between carbon nanotube walls". Chemical Physics Letters 317, 77-82.
- 133) <u>Terrones, M., Terrones, H., Grobert, N., Hsu, W. K., Zhu, Y. Q., Kroto, H. W., Walton, D. R. M., Kohler-Redlich, Ph., Rühle, M. Zhang, J.P., Cheetham, A.K. (1999), An efficient route to large arrays of CN, nanofibre by pyrolysis of ferrocene/melamine mixtures, *Applied Physics Letters* 75, 3932-3934.</u>
- 134) Blase, X., Charlier, J-C., De Vita, A., Car, R., Redlich, Ph., <u>Terrones, M.</u>, Hsu, W.K., Terrones, H., Carroll, D.L., Ajayan, P.M. (1999), "Boron-mediated growth of long helicity-selected carbon nanotubes". *Physical Review Letters*, 83, 5078, 5081.
- 135) Zhu, Y. Q., Hu, W.B., Hsu, W. K. <u>Terrones, M.</u>, Grobert, N., Hare, J. P., Kroto, H. W., Walton, D. R. M., Terrones, H. (1999) "SiC-SiO<sub>x</sub> heterojunctions in nanowires". *Journal of Materials Chemistry* 9, 3173-3178.
- 136) Grobert N., <u>Terrones, M.</u>, Redlich, Ph., Terrones, H., Escudero, R., Morales, F., Hsu, W.K., Zhu, Y.Q., Hare, J.P., Rühle, M., Kroto, H.W., Walton, D.R.M. (1999), Enhanced Magnetic Coercivities in Fe Nanowires, *Applied Physics Letters* 75 3366-3368.
- 137) Zhu, Y. Q., Hsu, W. K., <u>Terrones, M.</u>, Grobert, N., Hu, W. B., Hare, J. P., Kroto, H. W., Walton, D. R. M., Terrones, H. (1999), "Microscopy study of the growth process and structural features of silicon oxide nanoflowers". Chemistry of Materials 11, 2709-2715.
- 138) Tanaka, K., Endo, M., Takeuchi, K., Hsu, W.K., Kroto, H. W., <u>Terrones, M.</u>, Walton, D. R. M. (1999). "Large-Scale Synthesis of Carbon Nanotubes by Pyrolysis". In *The Science and Technology of Carbon Nanotubes* (Eds. K. Tanaka, T. Yamabe, K. Fukul): Chap. 12; pp 143-152 (Elsevier, Amsterdam).
- 139) Zhu, Y. Q., Hu, W. B., Hsu, W. K., <u>Terrones, M.</u>, Grobert, N., Hare, J. P., Kroto, H. W., Walton, D. R. M., Terrones, H. (1999), "Tungsten Oxide Tree-like Structures". *Chemical Physics Letters* 309, 327-334
- 140) Kohler-Redlich, Ph., <u>Terrones, M.</u>, Manteca-Diego, C., Hsu, W.K., Terrones, H., Rühle, M., Kroto, H.W., Walton, D.R.M. (1999), "Stable BC₂N nanostructures: Low temperature production of segregated C/BN layered materials". *Chemical Physics Letters* 310, 459-465.
- 141) <u>Terrones, M.</u>, Grobert, N., Hsu, W. K., Zhu, Y. Q. Hu, W. B., Terrones, H., Hare, J.P., Kroto, H. W., Walton, D. R. M. "Advances in the creation of filled nanotubes and novel nanowires". *Materials Research Society Bulletin* 24, 43-49.
- 142) Hsu, W. K, Trasobares, S., Terrones, H., <u>Terrones, M.</u>, Grobert, N., Zhu, Y. Q., Li, W. Z., Hare, J. P., Escudero, R., Kroto, H. W., Walton, D. R. M. (1998), "Electrolytic formation of carbon-sheathed mixed Sn-Pb nanowires". *Chemistry of Materials* 11, 1747-1751.
- 143) Zhu, Y. Q., Hsu, W. K., Hu, W. B., <u>Terrones, M.</u>, Grobert, N., Hare, J. P., Kroto, H. W., Walton, D. R. M., Terrones, H. (1999) "A simple route to generate silicon-based nanostructures". *Advanced Materials*.11, 844-847
- 144) <u>Terrones, M.,</u> Redlich, Ph., Grobert, N., Trasobares, S., Hsu, W. K., Terrones, H., Zhu, Y. Q., Hare, J. P., Cheetham, A. K., Rühle, M., Kroto, H. W. and Walton, D. R. M. (1999). "Carbon Nitride Nanocomposites: Formation of Aligned C<sub>x</sub>N<sub>y</sub> Nanofibres", *Advanced Materials* 11, 655-658.
- 145) Birkett, P. R. & Terrones, M. (1999); "Stretching the point". Chemistry in Britain 35, 45-48.
- Hsu, W. K. Zhu, Y. Q., Trasobares, S., <u>Terrones, M.</u>, Grobert, N., Terrones, H., Takikawa, H., Hare, J. P., Kroto, H. W., Walton, D. R. M. (1999); "Solid phase production of carbon nanotubes". *Applied*

Physics A 68, 493-495.

- 147) Hsu, W. K., Li, J., <u>Terrones, M.</u>, Terrones, H., Grobert, N., Zhu, Y. Q., Trasobares, S., Hare, J. P., Pickett, C. J., Kroto, H. W., Walton, D. R. M. (1999); "Electrochemical Production of Low-melting Metal Nanowires". *Chemical Physics Letters* 301, 159-166.
- 148) Fowler, P. W., Rogers, K. M., Selfert, G., <u>Terrones, M.</u>, Terrones, H. (1999); "Pentagonal rings with nitrogen excess in BN cages and nanotubes". *Chemical Physics Letters* 299, No. 5, 359-367.
- 149) <u>Terrones, M.,</u> Hsu, W. K., Kroto, H. W., Walton, D. R. M. (1998): "Nanotubes: A Revolution in Material Science and Electronics". In *Fullerenes and Related Structures*; Topics in Chemistry Series, Ed. A. Hirsch (Springer-Verlag), vol. 199, ch. 6, pp.189-234.
- 150) Grobert, N., <u>Terrones, M.</u>, Osborne, A. J., Terrones, H., Hsu, W. K., Trasobares, S., Zhu, Y. Q., Hare, J. P., Kroto, H. W., Walton, D. R. M. (1998): "Thermolysis of C<sub>∞</sub> thin films yields Ni-filled tapered nanotubes". *Applied Physics A* 67, 595-598.
- 151) Zhu, Y. Q., Hsu, W. K., <u>Terrones, M.</u>, Grobert, N., Terrones, M., Hare, J. P., Kroto, H. W., Walton, D. R. M. Walton. (1998): "3D Silicon oxide nansotructures; from nanoflowers to radiolaria". *Journal of Materials Chemistry* 8, 1859-1864.
- 152) <u>Terrones, M.</u>, Hsu, W. K., Ramos, S., Castillo, R., Terrones, H. (1998): "The Role of Boron Nitride in graphite plasma arcs". Fullerene Science & Technology 6, 787-800.
- 153) Terrones, H., & <u>Terrones, M.</u> (1998): "Fullerenes with Non-positive Gaussian Curvature: Holey Balls". Fullerene Science and Technology 6, 751-768.
- 154) Terrones, H. and <u>Terrones, M.</u> (1998): "Fullerenes and Nanotubes with Non-Positive Gaussian Curvature". *Carbon* 36, 725-730.
- 155) Dunne, L. J., Nolan, P., Munn, J., <u>Terrones, M.</u>, Jones, T., Kathirgamanathan P., Fernandez, J. (1998): "Formation of Fullerene-related cage structures during flaming combustion of polymers". *Combustion and Flame* 114, 591-593.
- 156) Zhu, Y. Q., Sekine, T., Kobayashi, T., Takazawa, E., <u>Terrones, M.</u>, Terrones, H. (1998): "Collapsing Carbon Nanotubes and Diamond formation under Shock waves". *Chemical Physics Letters* 287, 689-693.
- 157) Heggie, M. I., <u>Terrones, M.</u>, Eggen, B. R., Jungnickel, G., Jones, R., Latham, C. D., Briddon, P. R., Terrones H. (1998): "Quantitative Density Functional Study of Carbon Onions". *Physical Review B*. 57, 13339-13342.
- 158) Terrones, M., Grobert, N., Zhang, J. P., Terrones, H., Olivares, J., Kordatos, K., Hsu, W. K., Hare, J. P., Prassides, K., Cheetham, A. K., Kroto, H. W. and Walton, D. R. M. (1998): "Formation of aligned carbon nanotubes catalysed by laser-etched cobalt thin films". Chemical Physics Letters 285, 299-305.
- 159) Hsu, W. K., <u>Terrones, M.</u>, Terrones, H., Grobert, N., Kirkland, A. I., Hare, J. P., Prassides, K., Townsend, P. D., Kroto, H. W., Walton, D. R. M. (1998): "Electrochemical Formations of Novel Nanowires and their Dynamic Effects". *Chemical Physics Letters* 284, 177-183.
- 160) Terrones, M., Hsu, W. K., Schilder, A., Terrones, H., Grobert, N., Hare, J. P., Zhu, Y. Q., Schwoerer, M., Prassides, K., Kroto, H. W., Walton, D. R. M. (1998): "Novel Nanotubes and Encapsulated Nanowires". Applied Physics A 66 307-317.
- 161) Terrones, H. and <u>Terrones M.</u> (1997): "The transformation of Polyhedral Particles into Graphitic Onions". Journal of Physics and Chemistry of Solids 58, 1789-1796.
- Dunne, L. J., Nolan, P. F., Munn, J., <u>Terrones, M.</u>, Jones, T., Kathirgamanathan P., Fernandez, J., Hudson, A. D. (1997): "Experimental Verification of the Dominant Influence of Extended Carbon Networks on the Structural, Electrical and Magnetic Properties of a Common Soot". *Journal of Physics: Condensed Matter* 9, 10661-10673.
- 163) Ricardo-Chávez, J. L., Dorantes-Dávila J., <u>Terrones, M.</u>, and Terrones, H. (1997): "Electronic Properties of Novel Fullerene-related Structures with Non-positive Gaussian Curvature: Finite Zeolites". *Physical Review B* 56, 12143-12146.
- 164) <u>Terrones, M.</u> Grobert, N., Olivares, J., Zhang, J. P., Terrones, H., Kordatos, K., Hsu, W. K., Hare, J. P., Kroto, H. W., Prassides, K., Cheetham, A. K., Townsend, P. D., Walton, D. R. M. (1997): "Controlled Production of aligned-nanotube bundles". *Nature* 388, 52-55.
- 165) Terrones, H. & <u>Terrones M.</u> (1997): "Quasiperiodic Icosahedral Graphite Sheets and High Genus Fullerenes with Non Positive Gaussian Curvature". *Physical Review B*, 55, 9969-9974.
- 166) <u>Terrones, M.,</u> Hsu, W. K., Hare, J. P., Kroto, H. W., Walton, D. R. M. (1997): "Synthetic Routes to Novel Nanomaterials". Fullerene Science & Technology 5, 813-827.
- 167) Hsu, W. K., <u>Terrones, M.</u>, Hare, J. P., Terrones, H., Kroto, H. W., Walton, D. R. M. (1996): "Electrolytic Formation of Carbon Nanostructures". *Chemical Physics Letters*, 261, 161-166.
- 168) Terrones, M., Hsu, W. K., Terrones, H., Zhang, J. P., Ramos, S., Hare, J. P., Castillo, R., Prassides, K., Cheetham, A. K., Kroto, H. W., Walton, D. R. M. (1996): "Metal Particle Catalysed Production of Nanoscale BN Structures" Chemical Physics Letters. 259, 568-573.
- 169) Terrones, M., Benito, A. M., Manteca-Diego, C., Hsu, W. K., Osman, O. I., Hare, J. P., Reid, D. G., Terrones, H., Cheetham, A. K., Prassides, K., Kroto, H. W., Walton, D. R. M. (1996): "Pyrolytically Grown B.C.N. Nanostructures: Nanofibres and Nanotubes. Chemical Physics Letters 257, 576-582.
- 170) Terrones, M., Hsu, W. K., Hare, J. P., Walton, D. R. M., Kroto, H. W. and Terrones H. (1996): "Graphitic Structures: from planar to spheres, toroids and helices", *Philosophical Transactions Royal Society A* 354, 2055-2054.
- 171) Hare, J. P., Hsu, W. K., Kroto, H. W., Lappas, A., Prassides, K., <u>Terrones, M.</u> and Walton, D. R. M. (1996): "Nanoscale encapsulation of molybdenum carbide in carbon clusters". *Chemistry of Materials*, 8, 6-8.

- 172) <u>Terrones, M.</u> and Terrones H. (1996): "The role of defects in Graphitic Structures". Fullerene Science and Technology 4, 517-533.
- 173) Hare, J. P., Hsu, W. K., <u>Terrones, M.</u>, Sarkar, A., Firth, S. G., Lappas, A., Abeysinghe, J. R., Kroto, H. W., Prassides, K., Taylor, R. and Walton D. R. M. (1996): "Fullerene-Based Materials Science at Sussex". *Molecular Materials* 7, 17-22.
- 174) Hsu, W. K., Hare, J. P., <u>Terrones, M.</u>, Kroto, H. W., Walton, D. R. M., Harris, P. J. F. (1995): "Condensed-phase nanotubes". *Nature* 377, 687.
- 175) Terrones, H., <u>Terrones, M.</u> and Hsu, W. K. (1995): "Beyond C<sub>60</sub>: Graphite structures for the future". Chemical Society Reviews 24, 341-350.
- 176) Kroto, H. W., Hare, J. P., Sarkar, A., Hsu, K., <u>Terrones. M.</u> and Abeysinghe, J. R. (1994): "New Horizons in Carbon Chemistry and Material Sciences". MRS Bulletin, 19, 51-55.

### D) Published contributions to academic conferences

- <u>Cruz-Silva, E., Lopez-Urias, F., Munoz-Sandoval, E., Terrones, M.</u> (2005). "Tetrahedral magnetic cluster embedded in metallic matrix: Electron-correlation effects". *IEEE TRANSACTIONS ON MAGNETICS* 41, 3428-3430.
- Terrones, M., Terrones, H., Banhart, F., Charlier, J.-C., Ajayan, P.M. (2001). Connecting and joining single-walled carbon nanotubes. CARBON'01 (LEXINGTON, KENTUCKY USA, JULY 14-19, 2001).
- Mayne, M., Grobert , N., Terrones, M., Kamalakaran, R., Rühle, M., Walton, D.R.M. Kroto, H. W. (2001).
   High yield synthesis of carbon nanotube arrays by pyrolysis of benzene/metallocene aerosols.
   CARBON'01 (LEXINGTON, KENTUCKY USA, JULY 14-19, 2001).
- Grobert, N., mayne, M., Terrones, M., Sloan, J., Dunin-borkowski, R.E., Kamalakaran, R., Seeger, T., Terrones, H., Rühle, M., Walton, D.R.M. Kroto, H.W., Hutchison, J.L. (2001). Metal and alloy nanowires:iron and invar inside carbon nanotubes. CARBON'01 (LEXINGTON,KENTUCKY USA, JULY 14-19, 2001).
- Seeger, T., Kohler-Redlich, Ph., Grobert, N., <u>Terrones, M.</u>, Walton, D. R. M., Kroto, H. W., Rühle, M. (2000). Coating of Carbon Nanotubes. EUROCARBON 1, 473-474.
- Terrones, M., Terrones, H., Grobert, N., Trasobares, S., Hsu, W.K., Zhu, Y. Q., Hare, J. P., Kroto, H. W., Walton, D. R. M., Kohler-Redlich, Ph., Han, W. Q., Seeger, T., Rühle, M., Zhang, J. P., Cheetham, A. K. (2000). Efficient routes to Large arrays of CN<sub>x</sub> Nanofibres. EUROCARBON 1, 475-476.
- Grobert, N., Terrones, H., Hsu, W.K., Zhu, Y. Q., Walton, D. R. M., Kroto, H. W., <u>Terrones, M.</u>, Han, W. Q., Kohler-Redlich, Ph., Seeger, T., Rühle, M., Morales, F., Escudero, R. A novel route to Iron-filled Nanowires. EUROCARBON 2, 1033-1034.
- Muñoz-Navia, M. J., Dorantes Dávila, J., Guirado-López, R. A., Terrones, H., <u>Terrones, M.</u>, Grobert, N., Kroto, H. W., Walton, D. R. M. (2000) Papel Catalizador del Pd en Nanoestructuras de Carbón. Suplemento del Bol. Soc. Mex. Fis. 14-3, 10.
- Suplemento del Bol. Soc. Mex. Fis. 14-3, 10.

  Terrones H. & <u>Terrones M.</u> (1998): "Geometry and Energetics of High Genus Fullerenes and Nanotubes".

  DIMACS Technical Reports (Discrete Mathematics and Theoretical Computer Science Technical Reports), In press.
- 10) Grobert, N., Hare, J. P., Hsu, W. K., Kroto, H. W., Pidduck, A. J., Reeves, C. L., Terrones, H., <u>Terrones, M.</u>, Vizard, C., Wallis, D. J., Walton, D. R. M., Wright, P. J., Zhu, Y. Q. (1998): "Nanotechnology of Nanotubes and Nanowires: From aligned carbon nanotubes to silicon oxide nanowires". In *Electronic Properties of novel Materials Progress in Molecular Nanostructures*. Eds. H. Kuzmany, J. Fink, M. Mehring and S. Roth, American Institute of Physics Conference Proceedings 442, pp 25-28.
- 11) Grobert, N., <u>Terrones, M.</u>, O. J. Osbome, Terrones, H., Hsu, W. K., Trasobares, S., Zhu, Y. Q., Hare, J. P., Kroto, H. W., Walton, D. R. M. (1998): "Pyrolysis of C<sub>80</sub>-thin films yields Ni-filled sharp nanotubes". In *Electronic Properties of novel Materials Progress in Molecular Nanostructures*. Eds. H. Kuzmany, J. Fink, M. Mehring and S. Roth, American Institute of Physics Conference Proceedings 442, pp 29-33.
- 12) Heggle, M. I., <u>Terrones, M.</u>, Eggen, B. R., Jungnickel, G., Jones, R., Latham, C. D., Briddon, P. R. and Terrones, H. (1997): "LDF Calculations on Large Fullerenes and Onions". In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials, Vol. 4*, Eds. K. M. Kadish and R. S. Ruoff., Electrochemical Society, Pennington, N.J., pp. 1141-1150.
- 13) <u>Terrones, M.</u>, Hsu, W. K., Grobert, N., Terrones, H., Zhang, J. P., Hare, J. P., Kordatos, K., Prassides, K., Cheetham, A. K., Kroto, H. W. and Walton, D. R. M. (1997): "Production of Novel B<sub>x</sub>C<sub>y</sub>N<sub>x</sub> Nanomaterials and Metal Nanowires" in *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials, Vol. 4*, Eds. K. M. Kadish and R. S. Ruoff., Electrochemical Society, Pennington, N.J., pp. 825-842.
- 14) Rowlands, A. P., <u>Terrones, M.,</u> Townsend, P. D., Kordatos, K. (1997): "Radio-Thermoluminiscence Spectra of Fullerenes". In *Luminescent Materials VI*, Eds. C. R. Ronda and T. Welker, PV 97-29, Electrochemical Society, Pennington, N.J., pp. 129-140.
- 15) Ricardo-Chávez, J. L., Dorantes-Dávila, J., <u>Terrones, M.</u> and Terrones H. (1997): "Structure and Electronic Properties of High Genus Fullerenes with Nopn-Positive Gaussian Curvature". In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials, Vol. 4*, Eds. K. M. Kadish and R. S. Ruoff, Electrochemical Society, Pennington, N. J. pp. 662-702
- and R. S. Ruoff, Electrochemical Society, Pennington, N.J., pp. 692-702.
  16) Terrones, M., Grobert, N., Olivares, J., Kordatos, K., Hsu, W. K., Hare, J. P., Townsend, P. D., Prassides, K., Kroto, H. W. and Walton, D. R. M. (1997): "Controlled Production of Nanotubes Via Pyrolitic Techniques". In *Molecular Nanostructures*, Eds. H. Kuzmany, J. Fink, M. Mehring and S. Roth, World Scientific, pp.376-380.

17) Hsu, W. K., Terrones, M., Hare, J. P., Grobert, N., Kroto, H. W. and Walton, D. R. M. (1997); "The Electrochemical Formation of Nanowires". In *Molecular Nanostructures*, Eds. H. Kuzmany, J. Fink, M. Mehring and S. Roth, World Scientific, pp. 381-385.

18) <u>Terrones, M.</u>, Berito, A. M., Hsu, W. K., Osman, O. I., Hare, J. P., Reid, D. G., Prassides, K., Kroto, H. W., Walton, D. R. M., Manteca-Diego, C., Terrones, H. (1996): "Morphology Effects of Catalytic Particles in Pyrolytic Grown B.C.N. Nanofibres and Nanotubes". In Fullerene and Fullerene Nanostructures. Eds. H. Kuzmany, J. Finck, M. Mehring, S. Roth, World Scientific Publishing Co. Ltd., pp. 243-249.

 Hsu, W. K., <u>Terrones, M.</u>, Hare, J. P., Kroto, H. W., Walton, D. R. M. (1996): "Production of Carbon Nanotubes and Graphitic Onions by Condensed-Phase Electrolysis". In *Fullerene and Fullerene* Nanostructures, Eds. H. Kuzmany, J. Finck, M. Mehring, S. Roth, World Scientific Publishing Co. Ltd.,

DD.226-231

20) Terrones, M., Hare, J. P., Hsu, K., Kroto, H. W., Lappas, A., Maser, W. K., Pierik, A. J., Prassides, K., Taylor, R., Walton, D. R. M. (1995): "Physico-Chemical studies on nanotubes and their encapsulated compounds". In Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials, Vol. 2, Eds. K. M. Kadish and R. S. Ruoff., Electrochemical Society, Pennington, N.J., pp. 599-620.

### E) Book Reviews and other miscellaneous publications

Terrones, M. Terrones, H. "Nanotubos, Nanoestructuras y Nanocompuestos de Carbono: Los Materiales del Siglo XXI". Revista "Investigación y Clencia" - (Versión en Español de la Revista Scientific American), en prensa (2004).

2) Terrones, M. "La nanotecnología de Carbono". Artículo de revision invitado. Revista CIENCIA of the Mexican Academy of Science, vol- 5. No. pp. 30-39 (2002).

3) Terrones, M. "Composite Materials for Electronic Functions" (by D. D. L. Chung). Zeitschrift für Metallkunde, in press (2002).

4) Terrones, M. "Carbon Nanotubes and Related Structures: New materials for the XXI Century" (by P. J. F. Harris). Carbon 38, 787-788 (2000).

Terrones, M. (2001) "El universo de la Nanotecnología" (interview), Published in the Science section, 5)

La Jornada (Newspaper, pp III, January 22th. 2001).

Terrones, M., Terrones, H., Sabugal, P., (1998) "Fullerenos: ciencia juego y arte", Published in the 6)

Science and Technology section, El Nacional (Newspaper, pp 8-10, January 14th, 1998).

Terrones, H., <u>Terrones, M.</u>, (1998) "Fullerenos y Nanotubos de Carbono: Nuevos Materiales para el siglo XX1". Artículo de revisión invitado. Revista TIP especializada en Ciencias Químico Biológicas de 7) la Facultad de Estudios Superiores Zaragoza, in press. 8)

Terrones, M. (1998) "Nuevos Modelos en Investigación Clentifica". Artículo prsentado en el Foro México 2020: Retos y Perspectivas (Secretaria de Educación Pública, México D.F., 23 de Octubre

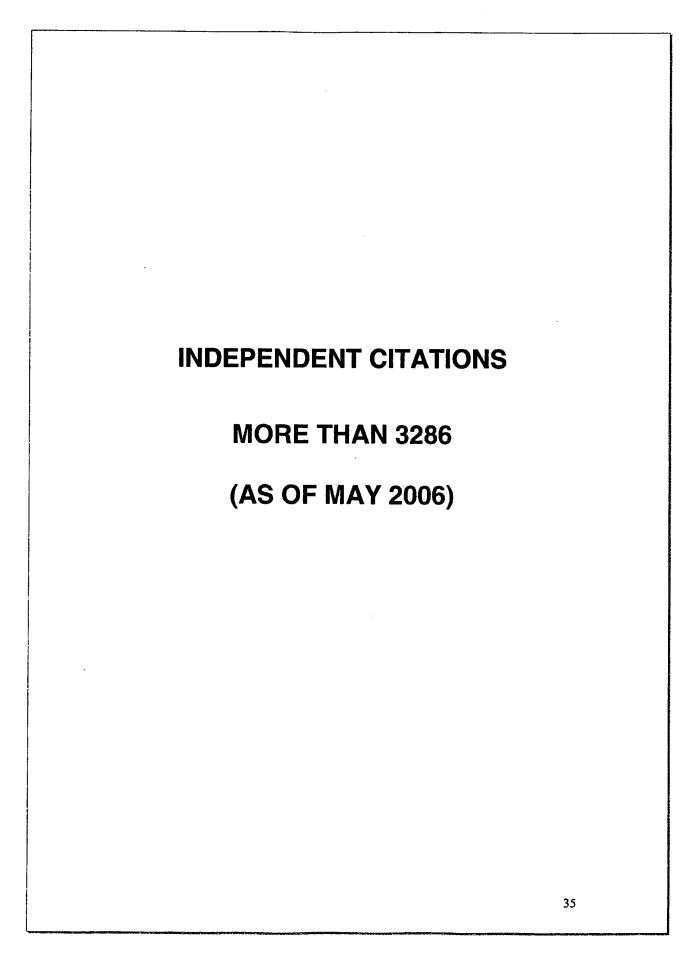
1998), CONACYT, México, .D.F. 1999, pp 261-280.

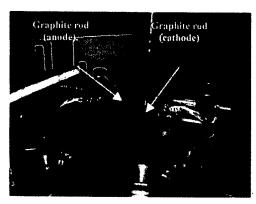
### X. REFEREE IN INTERNATIONAL JOURNALS

<ol> <li>Chemical Physics Letters</li> <li>Physical Review Letters</li> <li>Applied Physics Letters</li> <li>Advanced Materials</li> <li>Advanced Functional Materials</li> <li>Chemical Physics Physical Chemistry</li> <li>Carbon</li> <li>Chemistry of Materials</li> <li>Journal of Materials Chemistry</li> <li>Journal of Physical Chemistry</li> <li>Physical Review B (rapid)</li> <li>Chemical Communications</li> <li>Science</li> <li>Synthetic Metals</li> <li>Thin Solid Films</li> <li>European Journal of Physics B</li> </ol>	(45) (48) (31) (52) (8) (19) (80) (23) (48) (15) (18) (170) (2) (1) (3)
(Condensed Matter)	(1)

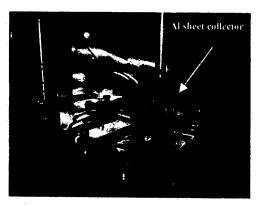
### XI. **REFEREE IN SUBJECT BOOKS**

- Graphite and Precursors (Ed. P. Delhaes)
   Carbon Nanotubes and Related Structures (P.J.F. Harris) Journal Carbon.
   Composite Materials for Electronic Functions (D. D. L. Chung) Journal Zeitschrift für Metallkunde.





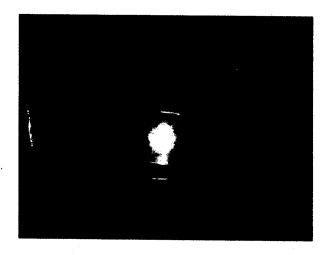
Position of the graphite rods for the resistive heating experiment. The anode showed a reduced diameter of 5 mm. The right rod exhibited a diameter of ¼ inch (cathode).



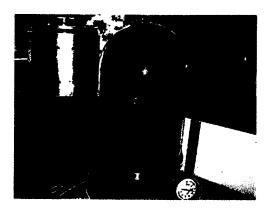
We used an aluminum sheet in a semicircle as a soot collector after the resisitive heating experiments.



Photograph of the experimental setup for the resistive heating experiments. The chamber was filled with helium at 100 torr pressure.



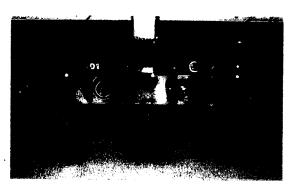
Photograph of the resistive heating experiment: Current:100 amps, reaction time: 1.52 minutes







View of the jar bell (top-left image) and interior chamber (top-right) after the resistive heating reaction, It is possible to observe the graphite rods and soot deposited over the bell jar and on the Al collector.





Photographs of soot collected form different parts of the chamber: A) sample collected from the plate; B) soot collected form the semicircular aluminum collector: C) carbon soot collected from the bell jar; D) graphite rod with reduced diameter (anode), see the "graphite crown" at the tip, and E) graphite rod (cathode) after the reaction.

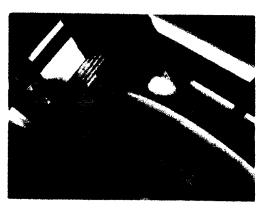


Position of the graphine reds in the left reduce in character had by 8 mm (anade), in the right rad with diameter of 10 mch (cathode)



We used an abinitium sheet in semicircle as a prophite and collector (substrate)

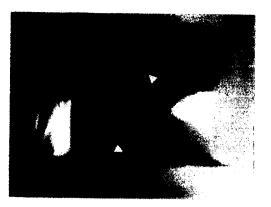




Left image show the excess dumentic filled and senting Helpin before the reasons in the image of the right we can use the among traped the expension in the party weight received.







After the reaction for both experiments, we can see the specimen (graphite soot) over the plate and coated the walks of the reactor



After remove the graphite soot by scraping A) specimen over the surface plate bottom, B) specimen coated the semicircle aluminum piece (the plate), C) graphite soot of the walls of interior reactor.

### IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Donald R. Huffman, et al. Examiner: Tsang Foster, S.N.

Serial No.: 08/236,933 Art Unit: 1745

Filed: May 2, 1994 Docket: 7913ZAZY

For: NEW FORM OF CARBON

Confirmation No.: 4115

Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

## DECLARATION OF ADAM DARWISH PURSUANT TO 37 C.F.R. §1.132

Sir:

### I, ADAM DARWISH, declare and say as follows:

- 1. I am currently a tutor of organic chemistry in the Chemistry Department at Sussex University, England. I was awarded a Ph.D. in Physical Organic Chemistry in 1992 and have continued working at Sussex University as a Research fellow until 1999, when I received a promotion to senior research fellow. I have conducted research in the area of fullerenes for several years. This research includes, but is not limited to, the preparation and purification of gram quantities of fullerenes, developing new fullerene-producing reactions, and improved chromatographic separation of C<sub>60</sub> and C<sub>70</sub>. I am appending hereto an abbreviated version of my curriculum vitae, which summarizes my experience in the fullerene area.
- 2. In preparing this Declaration, I have read and reviewed the contents of USSN 08/236,933 in its entirety ("'933 application"), especially the description therein of the

preparation of fullerenes, including  $C_{60}$  and  $C_{70}$ , and especially the procedure for separating the fullerenes from the soot described therein, especially in Example 1 thereof.

- 3. I was introduced to applicants' attorney by Dr. Harold Kroto.
- 4. I was requested by applicants' attorney to separate fullerenes, including  $C_{60}$  and  $C_{70}$ , from the soot sample prepared by Dr. Terrones, which was forwarded to me.
- The procedures described herein were either conducted by me or under my direct supervision and control.
- 6. The procedure used for separating the fullerenes from the soot utilized common separation techniques that were described in the '933 application or known and routine to one of ordinary skill in the art on August 30, 1990.
- 7. The same procedure was utilized for separating the fullerene from the soot produced at the lower pressure of 100 torr and at the higher pressure at 2 atm. More specifically, the samples of soot were extracted using a soxhlet extractor utilizing toluene as the solvent. Approximately, 10% of the soot sample was collected as soot extract. In the sample containing 1 gram of soot, i.e., the soot that was prepared from the vaporization of graphite at 100 torr using a current of about 100 amps, the soot extract was separated into the various fullerene fractions using preparative HPLC under the following conditions: Cosmosil 5µm PYE column (250mm x 10mm), HPLC-grade toluene as the solvent, eluted from the column at a rate of 4 ml/min. and the UV detector was set at 285 nm wavelength. Those fractions having an absorbance at 285 nm were collected. See Exhibit 2.
- 8. The fullerene fractions were then purified by recycling using the conditions described in Paragraph 7 herein.

- 9. A fullerene fraction, consisting of 65 mg of pure  $C_{60}$  crystals, another fullerene fraction consisting of 15 mg of  $C_{70}$  crystals and a third fullerene fraction of 7 mg of higher fullerenes comprised of  $C_{76}$  (1.2 mg),  $C_{78}$  (1.8 mg, two isomers)  $C_{84}$  (2.5 mg),  $C_{86}$  (0.5 mg), and  $C_{90}$  (1.0 mg, two isomers) together with  $C_{70}$ O (2 mg), were collected from the 1 gram of soot prepared from the vaporization of graphite at 100 torr using a current of about 100 amp. Each of the fractions contained enough material to be seen with the naked eye.
- 10. The identity of each of the fullerenes in each of the fractions was verified by the mass spectra.
- 11. I have attached hereto copies of the mass spectra of each of the fullerenes isolated from the vaporization of graphite at 100 torr using a current of about 100 amps and the HPLC tracings of each isolated fullerene. In addition, I have attached the photographs of samples of each of the separated fullerenes dissolved in toluene and photographs of the crystals of each of these fullerenes obtained from evaporation of exactly the half volume of the toluene solution obtained except for C<sub>86</sub> where all the toluene solution was evaporated to dryness. (see Exhibits 3-12).
- 12. Exhibit 3 includes the mass spectrum of a sample of C<sub>60</sub> (3)(a) and the HPLC tracing of the C<sub>60</sub> fraction (3)(b). Exhibit 3 further includes a photograph of a sample of C<sub>60</sub> in solution in toluene (3)(c) and a photograph of the C<sub>60</sub> crystals obtained from the evaporation of the toluene (3)(d). The mass spectrum confirmed the identity of the C<sub>60</sub>, and both the mass spectrum and the HPLC tracing showed that the product is quite pure. As indicated hereinabove, 65 mg of the C<sub>60</sub> crystals were recovered, which amount can be seen with the naked eye.

  Moreover, as further shown from the photograph in (3)(d), C<sub>60</sub> is present in sufficient amounts to be seen with the naked eye.

- 13. Exhibit 4 depicts the mass spectrum of the C<sub>70</sub> fraction (4)(a) and the HPLC tracing of the C<sub>70</sub> fraction (4)(b). The mass spectrum confirms the identity of C<sub>70</sub>, while the mass spectrum and the HPLC tracing show that the sample is quite pure (Exhibit 4). Exhibit 4 further includes a photograph of a sample of the C<sub>70</sub> dissolved in toluene (4)(c) and a photograph of C<sub>70</sub> after evaporation of the toluene (4)(d). As indicated hereinabove, 15 mg of C<sub>70</sub> were collected, which also can be seen with the naked eye. As further shown by the photograph in Exhibit (4)(d), the C<sub>70</sub> crystals were present in sufficient amounts to be seen with the naked eye.
- 14. The remaining fullerenes ("higher fullerenes") were present in a total amount of 9 mg, and the higher fullerenes in total were present in amounts sufficient to be seen with the naked eye.
- 15. Exhibit 5 shows the mass spectrum of C<sub>70</sub>O, the HPLC tracing of the product and a photograph of C<sub>70</sub>O solution in toluene. Again, the mass spectrum confirms the identity of the product, while the mass spectrum and HPLC tracing show that it is quite pure.
- 16. Exhibit 6 depicts the mass spectrum of C<sub>76</sub>, the HPLC tracing of C<sub>76</sub>, and a photograph of C<sub>76</sub> in solution in toluene. From the mass spectrum and the HPLC tracing, the product is quite pure. The mass spectrum confirms the identity of the product.
- 17. Exhibit 7 depicts the mass spectrum of C<sub>78</sub>, the HPLC tracing of the two isomers of C<sub>78</sub> that were obtained from the soot, and a photograph of C<sub>78</sub> in solution in toluene. The mass spectrum confirms that the product is C<sub>78</sub>, and the HPLC tracing clearly shows that 2 isomers were formed.
- 18. Exhibit 8 depicts the mass spectrum of  $C_{84}$ , the HPLC tracing of  $C_{84}$  and a photograph of  $C_{84}$  dissolved in toluene. The mass spectrum confirms the identity of the product as  $C_{84}$  and the mass spectrum and the HPLC tracing show that the product is quite pure.

- 19. Exhibit 9 depicts the mass spectrum of C<sub>86</sub>, the HPLC tracing of same, and a photograph of C<sub>86</sub> dissolved in toluene. The identity of the product is confirmed by the mass spectrum, and the mass spectrum and the HPLC tracing show that the product is quite pure.
- 20. Exhibit 10 depicts the mass spectrum of C<sub>90</sub>, the HPLC tracing of two isomers of C<sub>90</sub> and a photograph of C<sub>90</sub> dissolved in toluene. The mass spectrum confirmed the identify of the product and the HPLC tracing shows that two isomers of C<sub>90</sub> were collected.
- 21. Exhibit 11 is a photograph of various fullerenes, i.e, C<sub>60</sub>, C<sub>70</sub>, C<sub>76</sub>, C<sub>78</sub>, C<sub>84</sub>, C<sub>86</sub>, and C<sub>90</sub> (that were obtained from the soot produced from the vaporization of graphite at 100 torr) dissolved in toluene.
- 22. Exhibit 12 consists of photographs of higher fullerene products, which were isolated from the soot produced from the vaporization of graphite at 100 torr, in solution in toluene and the solids of same obtained from the evaporation of exactly the half volume of the toluene solution obtained except for C<sub>86</sub> where all the toluene solution was evaporated to dryness. The bottom portion of Exhibit 12 depicts each of these higher fullerene products. As can be seen by the photographs, the C<sub>76</sub>, C<sub>78</sub>, C<sub>84</sub>, C<sub>86</sub> and C<sub>90</sub> produced from the soot obtained from the vaporization of graphite at 100 torr can be seen with the naked eye.
- 23. I also separated the second sample comprised of 100 mg. of soot that was produced at the higher pressure of 2 atm using the same technique as described in Paragraphs 7 and 8. Toluene (100 ml) was used as the solvent for extraction using a soxhlet extractor, and 9 mg or 9% yield was obtained. The various products obtained from this soot are described in Paragraphs 24-26.
- 24. Attached as Exhibit 13 is the mass spectrum of C<sub>60</sub> and photographs of a sample of C<sub>60</sub> in solution in toluene obtained from the soot produced from the vaporization of graphite at

2 atm and the  $C_{60}$  crystals obtained from the evaporation of the toluene. The mass spectrum confirmed the identity of  $C_{60}$ . As shown by the photograph in Exhibit 13, the  $C_{60}$  isolated (5.0 mg) from the 100 mg. of soot received from Dr. Terrones can be seen with the naked eye.

- 25. Attached as Exhibit 14 is the mass spectrum of  $C_{70}$ , and the photographs of a sample of  $C_{70}$  in solution in toluene obtained from the soot produced from the vaporization of graphite at 2 atm and  $C_{70}$  crystals (1.5 mg) obtained from the evaporation of the toluene. Again, as shown by the photograph, the  $C_{70}$  isolated from the 100 mg. of soot, which was sent by Dr. Terrones, can be seen with the naked eye.
- 26. Exhibit 15 depicts the mass spectrum of the higher fullerenes obtained when the vaporization of graphite was performed at 2 atm. The mass spectrum depicts that higher fullerenes up to C<sub>104</sub> were detected by the mass spectrum. Exhibit 15 also depicts the photographs of a sample of higher fullerenes in solution in toluene and photographs of the crystals of the higher fullerenes (1.0 mg) obtained after evaporation of toluene. Thus, the higher fullerenes in total were present in the soot obtained from the vaporization of graphite at 2 atm in amounts sufficient to be seen with the naked eye.
- Exhibit 16 consists of photographs of separate samples of  $C_{60}$ ,  $C_{70}$  and the higher fullerenes, isolated from the soot prepared from the vaporization of graphite at 2 atm and 100 amps, dissolved in toluene and photographs of the crystals of  $C_{60}$ ,  $C_{70}$  and the higher fullerenes obtained from evaporation of the toluene therefrom. Thus, as shown by the photographs, these crystals of  $C_{60}$ ,  $C_{70}$  and higher fullerenes can be seen with the naked eye.
- 28. I further declare that all statements made herein of my own knowledge are true and that alls statements made on information and belief are believed to be true and further that these statements were made with the knowledge that willful false statements and the like so

made are punishable by fine or imprisonment or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: August 28, 2007

Adam Darwish

### Curriculum Vitae

Name: Adam Darwish

Date of Birth: 7th March 1958

Gender: Male

Nationality: British

Marital Status: Married

Address: 15 Sunnydale Avenue, Patcham, Brighton, East Sussex, BN1 8NR

**Tel No.:** (Home) 01273 501522

(Mobile) 07810768880

E-mail: kapg2@sussex.ac.uk

### **EDUCATION**

D.Phil Physical Organic Chemistry (Sussex University, 1989-1992, UK)

BSc. / Chemistry (Yarmouk University, 1977-1980, Jordan)

### RESEARCH EXPERIENCE

2006-Present Tutor of Organic Chemistry, Chemistry Department, Sussex

University.

1999-2006 Senior Research Fellow, Chemistry Department, Sussex University.

1992-1999 Research Fellow, Chemistry Department, Sussex University

Research involved the preparation and purification of gram quantities of fullerenes, and development of a new fullerene-producing reactor together with improved chromatographic separation of  $C_{60}$  and  $C_{70}$ . Carrying out a number of studies into new chemical reactions of  $C_{60}$ ,  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$  and  $C_{84}$  and fluorinated fullerenes ( $C_{60}F_{18}$ ,  $C_{60}F_{18}O_x$  and  $C_{60}F_{20}$ ). These included reduction, oxidation, fluorinations, additions, electrophilic and nucleophilic addition/substitutions, which have resulted in a large number of publications (71 publications) in a variety of scientific journals.

1989-1992 D.Phil research student (gas phase elimination of some nitrogen-

### containing heteroaromatics)

### SELECTED PUBLICATIONS

- Fullerenes, Adam D. Darwish, Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem., 2007, 103, 370 – 391.
- Pyrolytic Trifluoromethylation of [76]-, [78]-, [84]-, and Aza[60]Fullerene with silver Trifluoroacetate; Evidence for Coordination of Fullerenes to Silver, Adam D. Darwish, A. K. Abdul-Sada, and R. Taylor, Fullerene, Nanotubes, and Carbon Nanostructures, 2006, 14(1), 111.
- 3. Isolation of Two Seven-membered Ring C58 Fullerene Derivatives: C<sub>58</sub>F1<sub>7</sub>CF<sub>3</sub> and C<sub>58</sub>F<sub>18</sub>. P. A. Troshin, A. G. Avent, A. D. Darwish, N. Martsinovich, A. K. Abdul-Sada, J. M. Street and R. Taylor, *Science*, 2005, 309, 278.
- Electrophilic Substitution by the Fluorofullerene C<sub>60</sub>F<sub>18</sub>, A. D. Darwish, A. G. Avent, A. K. Abdul-Sada, I. V. Gol'dt, I. Kuvytchko, P. B. Hitchcock and R. Taylor, Chem Eur. J., 2004, 10, 4523.
- Electrophilic Substitution of C<sub>60</sub>F<sub>18</sub> into Phenols: HF Elimination Between OH and a 1,3-Shifted Fluorine Giving
  Benzofurano[2',3':10,26]hexadecafluoro[60]fullerene and Derivatives, A. D. Darwish, A. G. Avent, J. M. Street and R. Taylor, Org. Biomol. Chem., 2003, 1, 1764.
- C<sub>60</sub>F<sub>20</sub>: "Saturnene", an Extraordinary Squashed Fullerene.
   V. Boltalina, V. Yu. Markov, P. A. Troshin, A. D. Darwish, J. M. Street and R. Taylor, Angew. Chem. Int. Ed., 2001, 40, 787.
- Novel Base-Catalysed Formation of Benzo[b]furano[60]- and -[70]Fullerenes.
   A.D. Darwish, A.G. Avent, H.W. Kroto, R. Taylor and D.R.M. Walton, J. Chem Soc., Perkin Trans. 2, 1999, 1983.
- Hydrogenation of [76]-, [78]- and [84]Fullerenes.
   A.D. Darwish, H.W. Kroto, R. Taylor and D.R.M. Walton, J. Chem Soc., Perkin Trans. 2, 1996, 1415.
- Preparation and 13C NMR Spectroscopic Characterization of C60Cl6.
   P.R. Birkett, A.G. Avent, A.D. Darwish, H.W. Kroto, R. Taylor and D.R.M. Walton, J. Chem Soc., Chem. Commun., 1993, 1230.





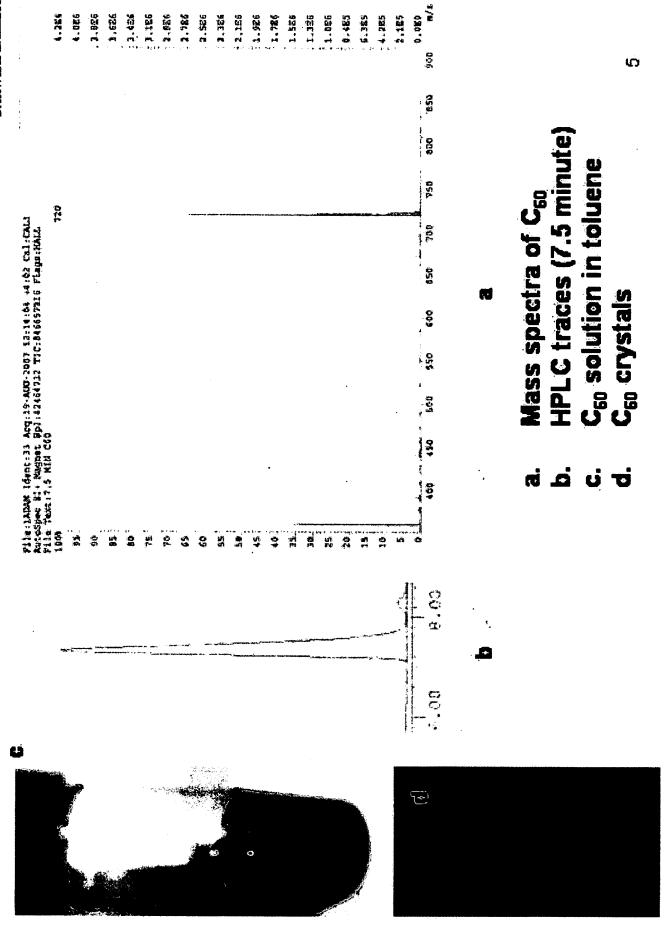


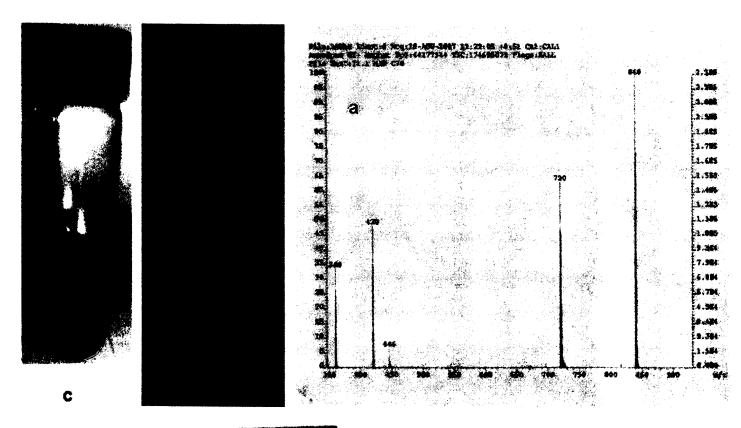






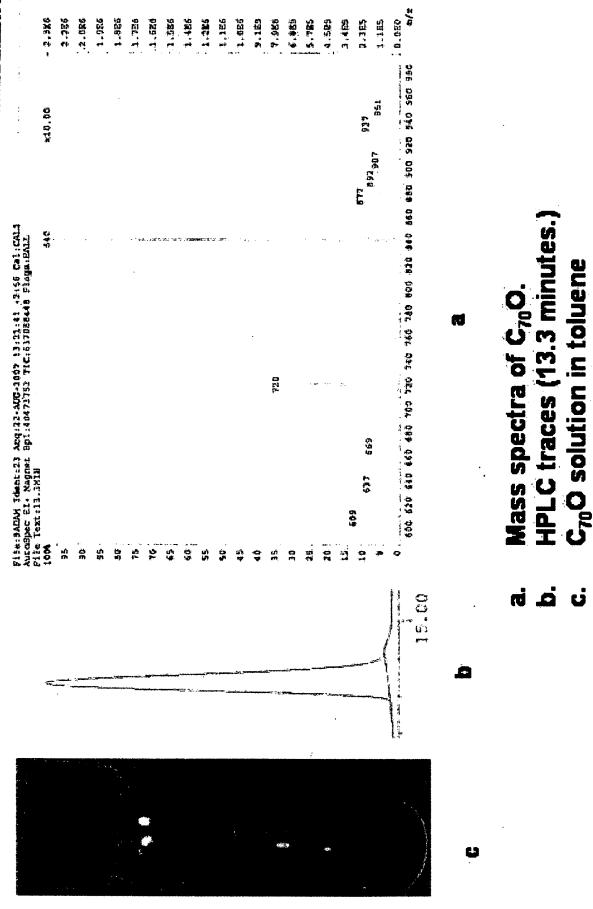
Concentrated soot extract in 30ml of toluene Soot extract in 100ml of toluene Soxhlet extractor வ ப் ப்

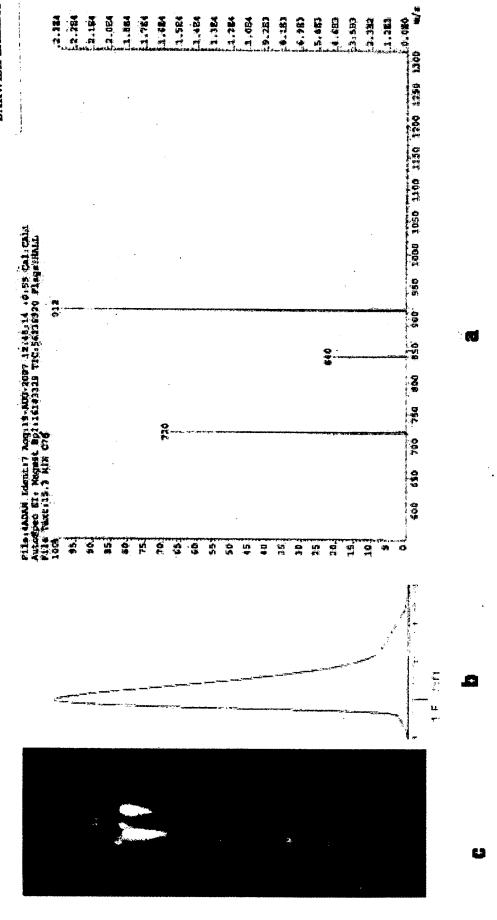




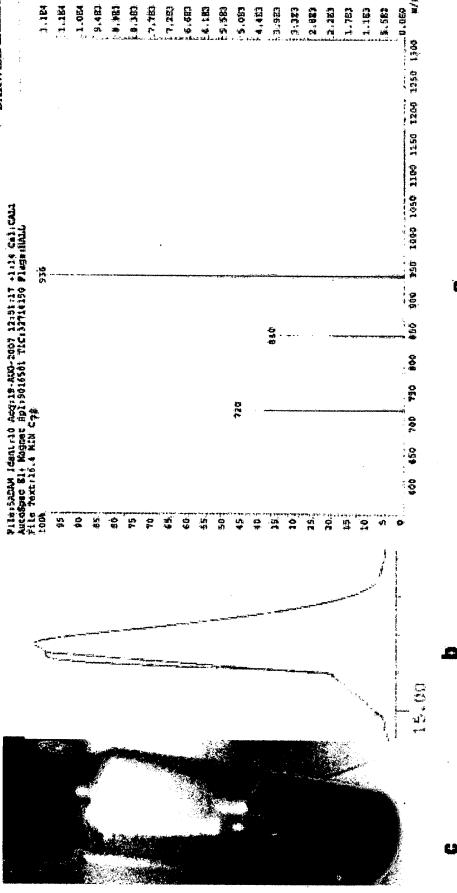


- Mass spectra of  $C_{70}$ HPLC traces (11.1 minutes)  $C_{70}$  solution in toluene  $C_{70}$  crystals a. b.
- c.
- d.



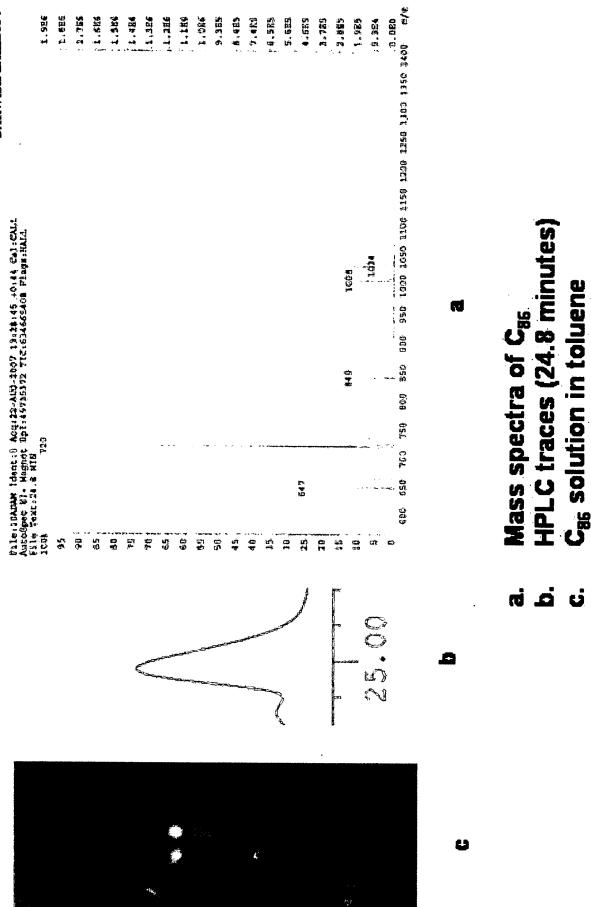


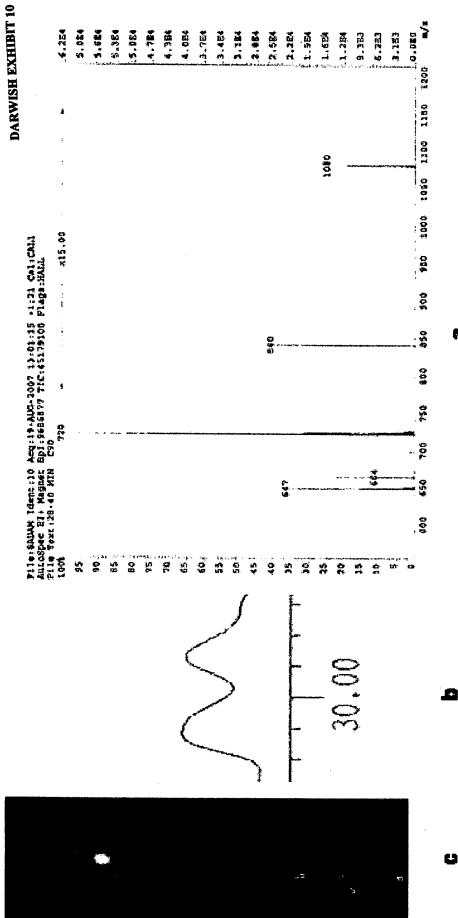
a. Mass spectra of C<sub>76</sub>
 b. HPLC traces (15.3 min.)
 c. C<sub>76</sub> solution in toluene



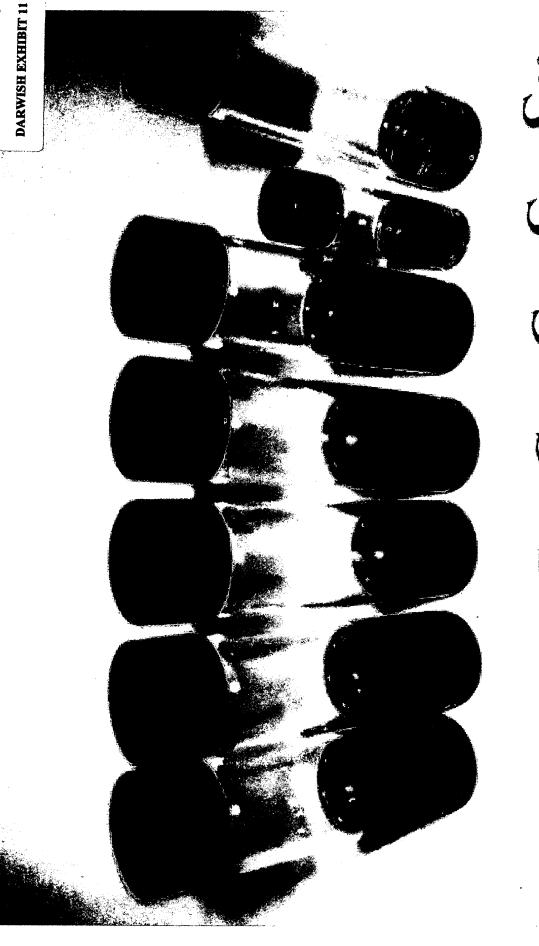
HPLC traces (16.4 & 16.7.3 min.), two isomers C<sub>78</sub> solution in toluene. Mass spectra of C78 æ ۵

Mass spectra of  $C_{B4}$ HPLC traces (20.5 min.) C<sub>84</sub> solution in toluene ئم ιċ

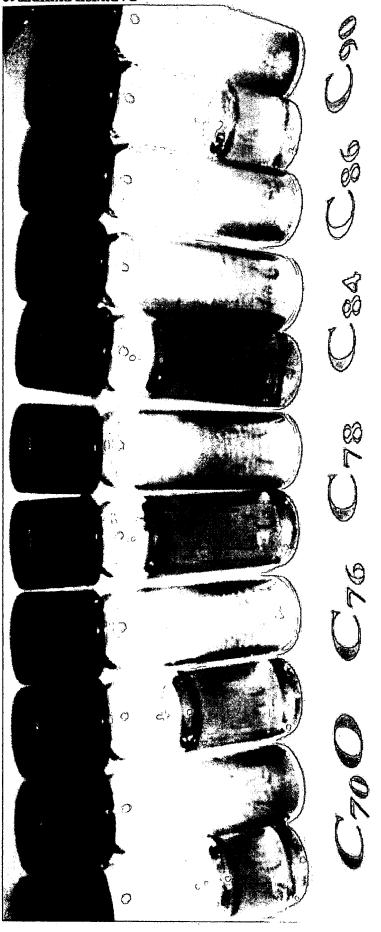


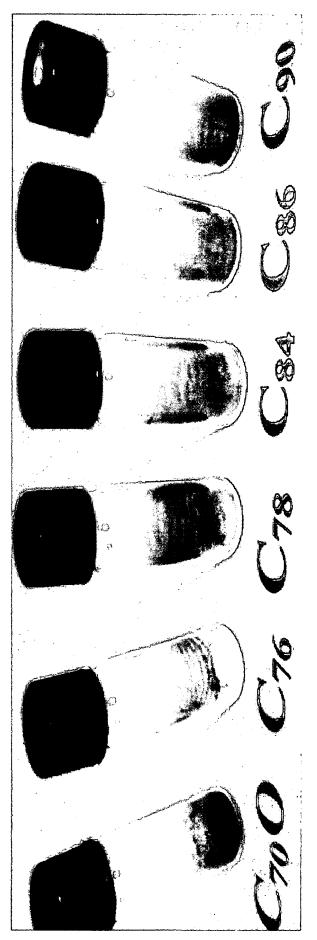


HPLC traces (29 & 31minutes), two isomers C<sub>20</sub> solution in toluene Mass spectra of C<sub>90</sub> ف.



760 C70 C76 C78 C84 C86 C90





0 \$ 7 50 20 5 0

## Mass spectra of Cen

# C<sub>60</sub> solution in toluene C<sub>60</sub> crystals

5

96

u) u)

un Vi

5

9 មា 30

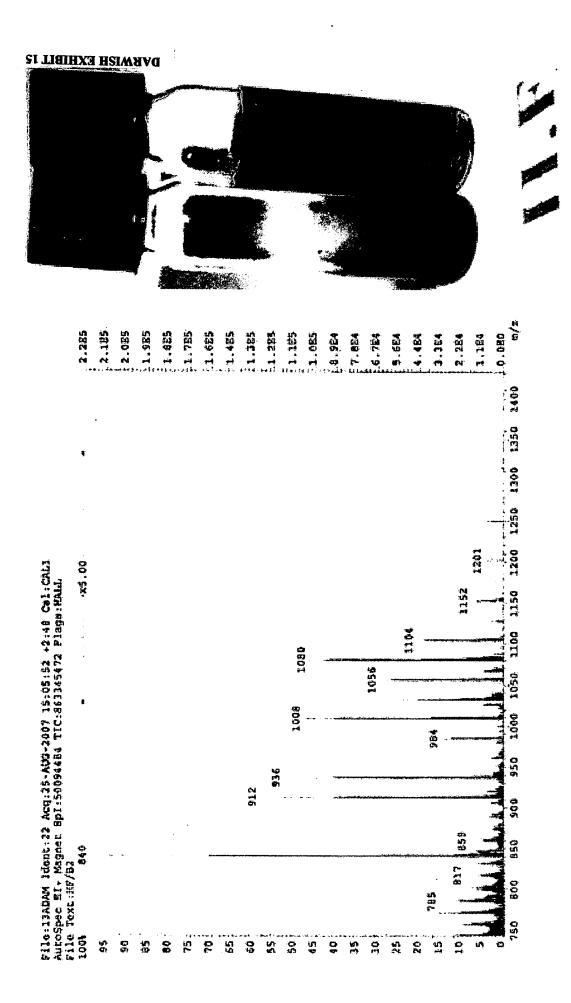
in N

0

# C<sub>70</sub> solution in toluene C<sub>70</sub> crystals

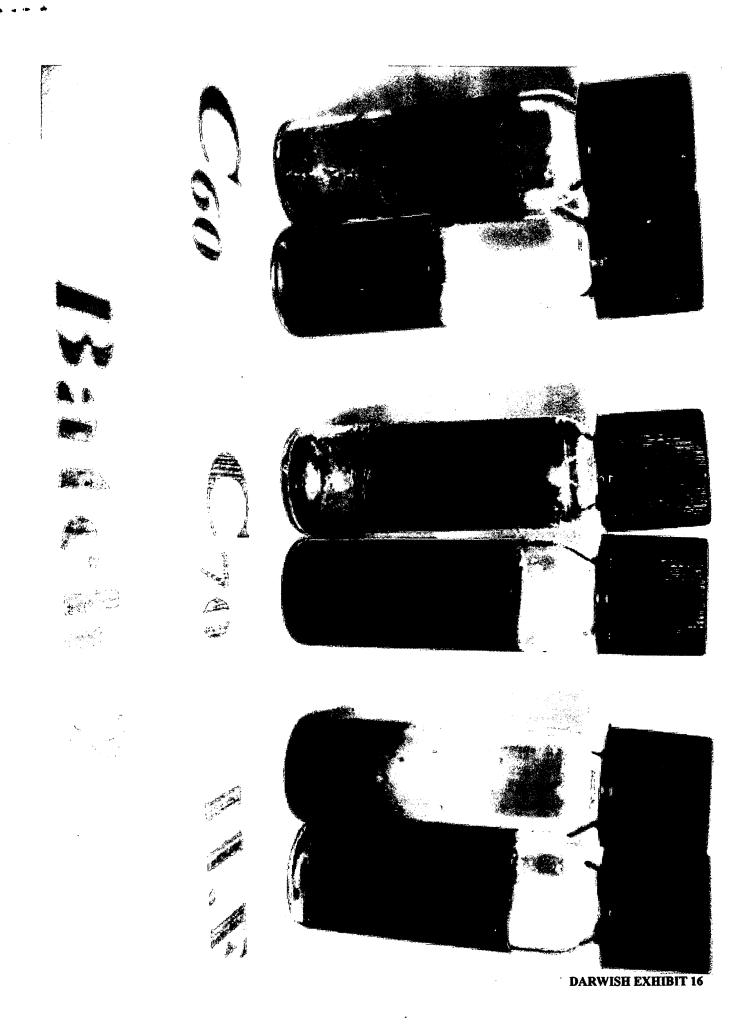
Mass spectra of C<sub>70</sub>

20



Mass spectra of H.F's up to C<sub>104</sub>

H.F's solution in toluene H.F's crystals



## PATENT OFFICE DATE STAMP WILL ACKNOWLEDGE RECEIPT OF:

- General Transmittal Letter (in duplicate)
- Communication
- Declaration of Harold W. Kroto Pursuant to 37 C.F.R. §1.132 (Exhibits 1-13)
- Declaration of Mauricio Terrones Pursuant to 37 C.F.R. §1.132 (Exhibits 1-3)
- Declaration of Adam Darwish Pursuant to 37 C.F.R. §1.132 (Exhibits 1-16)
- 6. Certificate of Mailing dated 9/4/07

Applicants: Donald R. Huffman, et al.

07/580,246 Serial No.:

Filed:

September 10, 1990

NEW FORM OF CARBON. For:

7913Z Docket:

September 4, 2007 Dated:

MJC:dg



### IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Donald R. Huffman, et al.

**Examiner:** 

Susy N. Tsang-Foster

Serial No.:

07/580,246

**Art Unit:** 

1745

Filed:

September 10, 1990

Docket:

7913Z

For:

NEW FORM OF CARBON

Dated:

October 12, 2007

Confirmation No. 5441

Mail Stop Amendment Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

### **DECLARATION**

Sir:

- I, Mark J. Cohen, hereby declare and state that:
- I am a member of the firm Scully, Scott, Murphy & Presser, located at 400
   Garden City Plaza, Garden City, NY 11530 and having a telephone number (516)
   742-4343. I am a patent attorney registered to practice before the USPTO and am acting in a representative capacity before the USPTO in the above-identified application.
- 2. An Office Communication relative to the above-identified application was issued on June 8, 2007 ("Office Communication"). A response was due on September 8, 2007. Since September 8 was a Saturday, the actual due date was September 10, 2007.
- 3. In response to the Official Communication, I had caused a copy of the documents annexed hereto in Exhibit A to be deposited with the United States Postal Service

as first class mail in a pre-paid envelope addressed to Mail Stop Amendment, Commissioner for Patents, P.O. Box 1450, Alexandria, Va 22313-1450. These documents made part hereof are listed hereinbelow.

۶,

- Transmittal Letter, which lists the Communication and the three
   Declarations identified in Items 2 and 4-6, hereinbelow, respectively.
- Communication dated September 4, 2007, referring to the Declarations in Items 4-6 hereinbelow.
- Certificate of Mailing dated September 4, 2007 as part of the Transmittal
   Letter and Communication referred to in Items 2 and 3.
- 4. A Declaration of Harold W. Kroto pursuant to 37 C.F.R. §1.132 executed on August 27, 2007, having 13 exhibits attached thereto\*
- 5. Declaration of Mauricio Terrones pursuant to 37 C.F.R. §1.132, executed on August 28, 2007, having three exhibits attached thereto\*
- Declaration of Adam Darwish pursuant to 37 C.F.R. §1.132 dated August
   28, 2007, having 16 exhibits attached thereto\*
- 7. A postcard which lists the documents that were mailed on September 4, 2007
- 4. As evidence of the timely filing of the Response to the outstanding Office Action, attention is directed to the Certificate of Mailing located on the bottom of page 1 of the "Communication" and the Transmittal Letter. The Certificate of Mailing certifies that the Transmittal Letter identifying the Items accompanying it, <u>viz</u>. the Communication identified in Item 2 and Declarations identified in Items 4-6 were

It is to be noted that these declarations were also filed in three other applications. Reference in these declarations is Serial No. 08/236,933.

- deposited as first class mail addressed to the Commission of Patents on September 4, a few days prior to the actual due date of the Response to the Official Communication.
- 5. The Communication referred to Item No. 2 and three Declarations referred to in Items 4-6 constitute a complete response to the Official Communication dated June 8, 2007.
- 6. Thus, the record indicates that a complete Response was filed prior to the due date on September 4, 2007 not only on time but also that it was filed.
- 7. As further evidence that the contents of the aforesaid envelope were timely mailed, attention is directed to the back of the postcard annexed hereto as Exhibit B. The postcard was also placed in the envelope with the other documents listed in Items 1-6 hereinabove that was addressed to the Commissioner of Patents on September 4, 2007. As clearly seen in Exhibit B, the postcard lists all of the items, which accompanied it in the mailing to the USPTO on September 4, 2007. Moreover, a review of the postcard clearly indicates a postmark date by the USPTO of September 7, 2007. This stamps evidence that not only was the Response to the Communication timely filed, but that the Response and the accompanying documents referred to in Paragraph 3 were received by the USPTO prior to the due date.
- 8. Thus, a complete Response to the Office Communication was timely filed and received by the USPTO.
- 9. I hereby declare that all statements made herein of my own knowledge are true, that all statements made on information and belief are believed to be true, and

further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application of any patent issuing thereon.

Dated

Mark J. Cohen

Registration No. 32,211